AN IN-DEPTH INVESTIGATION OF AN ALUMINUM CHLORIDE RETARDED MUD ACID SYSTEM ON SANDSTONE RESERVOIRS

A Thesis

by

NNENNA VALERIE ANETO

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2012

Major Subject: Petroleum Engineering

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Approved by:

Chair of Committee,	Hisham Nasr-El-Din
Committee Members,	Jerome Schubert
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ABSTRACT

An In-depth Investigation of an Aluminum Chloride Retarded Mud Acid System on Sandstone Reservoirs. (May 2012)

Nnenna Valerie Aneto, B.En., Federal University of Technology Owerri

Chair of Advisory Committee: Dr. Hisham Nasr-El-Din

Sandstone acidizing using mud acid is a quick and complex process where dissolution and precipitation occur simultaneously. Retarded mud acids are less reactive with the rock reducing the reaction rate hence increased penetration into the formation to remove deep damage.

To understand thoroughly the retarded mud acid system, an in-depth investigation of the reaction of HF (hydrofluoric) and H_2SiF_6 (fluorosilic acid) with alumino silicates and the retarded system is undertaken using coreflood analysis and mineralogy analysis using the inductively coupled plasma.

Coreflood analysis is used to understand and investigate the permeability changes in the sandstone rock as the retarded mud acid is injected at different conditions and the inductively coupled plasma (ICP) is used to investigate the effluent samples from the coreflood analysis to properly understand this system.

Several issues that have not been addressed previously in literature are identified and discussed, including an optimum flowrate when sandstone is acidized, by acidizing the sandstone rock with a retarded acid system at various flowrates and determining the initial and final permeabilities. Also investigated is the retarded acids compatibility with ferric iron and a comparison of the retarded acid system to regular acid to consequently enable a thorough understanding of the retarded mud acid system using aluminum chloride (AlRMHF).

Based on the work done, it is found that the absence of a hydrochloric (HCl) preflush is very detrimental to the sandstone core as calcium fluoride is precipitated and the retarded acid system is found to be compatible with iron(III) as an impurity. The regular acid (RMHF) dissolves considerably more silicon and produces more fines than the AlRMHF.

1cc/min is found to be the optimum flowrate when a sandstone core is acidized with AlRMHF. At this low flowrate, less silicon is dissolved, more aluminum is seen in the effluent and more calcium is dissolved. The retarded aluminum acid system considerably reduces the rate of reaction as evidenced in the dissolution reaction when compared to a regular mud acid system. This reduced rate of reaction implies deeper acid penetration and ultimately deeper damage removal.

DEDICATION

To God Almighty.

To my loving and supporting parents Mr and Mrs Aneto.

To my siblings Chichi, Tobenna, Agbomma, Uchenna, and Onyedikachi.

To the man that will be my husband.

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I would like to thank my advisor Dr. Nasr-El-Din for his unconditional support and encouragement throughout the period of my research. Under his supervision, I have increased, improved and harnessed my knowledge in production engineering – specifically, well stimulation on which he is an industry recognized expert.

I would also like to thank my committee members, Dr. Schubert and Dr. El-Halwagi, for their guidance and support throughout the course of this research.

A special thanks also to my colleagues in Dr. Nasr-El-Din's research group and the department faculty and staff for making my time at Texas A&M University great.

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Finally, a big thank you to my family for their encouragement, love, and support and to God Almighty through which all things are possible.

NOMENCLATURE

$AlCl_3$	Aluminum chloride
AlRMHF	Aluminum chloride retarded mud acid
HCl	Hydrochloric acid
HF	Hydrofluoric acid
HRMHF	Half regular mud acid
ICP	Inductively coupled plasma
RMHF	Regular mud acid

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CHAPTER I

INTRODUCTION

1.1 ACIDIZING

Well stimulation is a treatment performed on an oil or gas well to restore or enhance well productivity by improving the flow of hydrocarbons from the drainage area into the well bore. Acidizing is a well stimulation technique which involves the pumping/ placement of acid into the formation to remove well-bore damage. Acid effectiveness in well stimulation is derived from their ability to dissolve formation damaging/ formation plugging materials. By dissolving acid soluble components which include but are not limited to organic and inorganic scale, within underground rock formations or by the removal of material at the wellbore face, the rate of flow of oil and or gas out of production wells or the rate of flow of oil-displacing fluids into injection wells may be increased.

Any down-hole activity disturbs the thermodynamic equilibrium of the formation inadvertently causing formation damage. Formation damage specifically refers to obstructions occurring in the near-wellbore region of the rock matrix. External operations which can induce damage include; drilling, well completion, production, work-over operations, simulation treatment. Acidizing is an extremely sensitive process and its success is mostly dependent on the type of formation, additives used, and the

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This thesis follows the style of *SPE Journal.*

acidizing method chosen – these include matrix acidizing and acid fracturing. During acidizing, when acid is injected into a formation at pressures high enough to fracture the formation, this is termed acid fracturing. On the other hand, when this is applied at pressures below fracture pressure it is called Matrix acidizing.

1.2 MATRIX ACIDIZING

Matrix acidizing is the injection of an acid into the near-well bore formation area to enhance productivity by dissolving damaging materials/ reduce skin which maybe present ultimately recovering or enhancing reservoirs natural permeability without affecting the entire reservoir. The term “Matrix acidizing” is stemmed from the fact that the acid is injected into the matrix at pressures below the formation fracture pressure.

Matrix acidizing is a low-budget and low-volume operation when compared to high pressure fracturing, and is very advantageous for wells which are appropriate candidates. It is also important to note that matrix acidizing is of little benefit to undamged wells and would not enhance a reservoirs natural permeability.

1.3 ACID SYSTEMS

Acid systems to be used should be properly investigated and experimented before applying to any formation. Homogenous and heterogeneous formations react to different acids and acid additives in various ways, sometimes positive and others negative, so it is important to understand the reservoir characteristics of the formation, the specific reason

for the treatment and the implications of any acidizing treatment used. Acid systems currently in use can be broadly classified into; mineral acids, organic acids (powdered and dilute), mixed acids, and retarded acids. Common acids include; Hydrochloric acid (HCl), hydrofluoric acid, formic acid, acetic acid, sulfamic acid, chloroacetic acid, gelled acids, emulsified acids among others. Almost all acid treatments would have some amount of HCl. Usually, it is used as 15% by weight which is called regular acid. Lower concentrations are used when acid dissolving power is not the main acidizing consideration and higher concentrations are used when adequate corrosion inhibitors are readily available.

All acidizing treatments planned for well stimulation would require some concentration of corrosion inhibitors to protect well tubular from acid attack. Other additives/ minerals are also added for various reasons depending on the objective of the acid treatment. Other additive functions include; wettability alteration, friction reducers, acid diversion, reduces leak-off rate, sludge prevention/breakers, emulsion elimination, complexing agents (to complex iron to prevent precipitation), and cleanup additives. Careful decision making based on formation type, reservoir heterogeneity, past experience and oil field chemistry determine necessary additives for a planned acid job.

1.4 SANDSTONE ACIDIZING

Sandstones are sedimentary rocks composed mainly of quartz and/or feldspar. These sands are cemented together by a combination of any of feldspar, carbonates, clays

and/or silica. Sandstones account for about 30% of the world's petroleum reserves. The most common carbonates found in sandstone reservoirs are limestone, dolomite and siderite while the most common clays are kaolinite, illite, chlorite and montmorillonite. Feldspars occur in various forms. Fig. 1.1 shows the various components of sandstone.

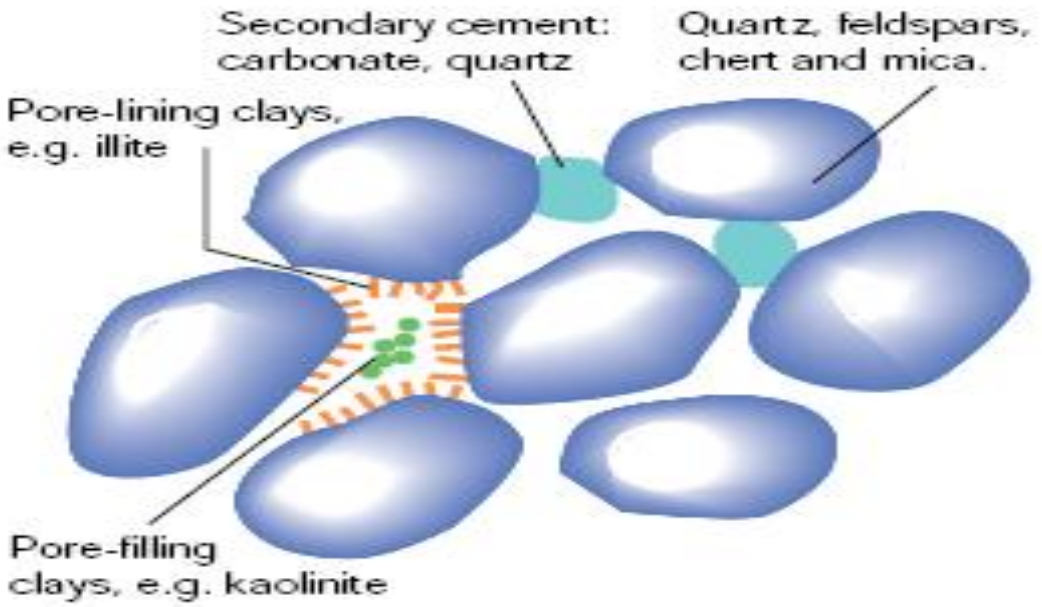

Fig. 1.1 Components of sandstone

Due to their complex mineralogy and acid/rock interaction, sandstone acidizing is a very sensitive procedure. Conventionally, sandstones are acidized almost exclusively with a mixture of HCl and HF commonly termed mud acid at various concentrations. HCl dissolves the carbonates and would for most cases leave no precipitates.

Limestone: $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$

Dolomite: $4HCl + CaMg(CO_3)_2 \rightarrow CaCl_2 + MgCl_2 + 2H_2O + 2CO_2$

Siderite: $2HCl + FeCO_3 \rightarrow FeCl_2 + H_2O + CO_2$

HF on the other hand would dissolve the silica, feldspars and clays (siliceous) present in the sandstone rock.

Silica: $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$

(silicon tetrafluoride)

$SiF_4 + 2HF \rightarrow H_2SiF_6$

(fluosilicic acid)

Kaolinite: $Al_4Si_4O_{10}(OH)_8 + 24HF + 4H^+ \rightarrow 4AlF_2 + 4SiF_4 + 18H_2O$

Montmorillonite: $Al_4Si_8O_{20}(OH)_4 + 40HF + 4H^+ \rightarrow 4AlF_2 + 8SiF_4 + 24H_2O$

Feldspars: $KAlSi_3O_8 + 14HF + 2H^+ \rightarrow K^+ + AlF_2 + 3SiF_4 + 8H_2O$

where K is magnesium, sodium or potassium.

Since the first successful practical application of sandstone acidizing, it has consisted of three main stages:

- A preflush, typically with hydrochloric acid to displace resident water and remove cementing carbonates such as calcite.
- A main acid stage of hydrochloric and hydrofluoric acids, used to dissolve feldspars, clays and other near-wellbore damaging materials.
- An afterflush, which may consist of anything such as hydrochloric acid, non-damaging ammonium chloride salts, organic acid, mutual solvents etc. depending on the chemistry and history of the reservoir. It is used mainly to displace the mud acid stage into the formation and to clean up reaction byproducts.

Conventionally, sandstones are acidized with mud acid but relatively poor results have been observed, which is mainly a result of:

- Secondary and tertiary precipitation caused by acidizing products, inadequate volumes of acid being used or poor design jobs.
- Due to the reservoir heterogeneity and permeability variation, the main acid stage could end up in a higher-permeability zone leaving the zone of interest unacidized.
- Mud acid is a very fast acting acid and could deconsolidate the rock in the near-wellbore region leading to the production of unwanted fines. (Tuedor et al. 2006)
- A large number of wells around the world are producing optimally due to successful acidizing treatment and there is therefore a need to find and improve methods to successfully acidize producing wells.

Mud acid due to the presence of HCl is a very fast acting acid. This rapid reaction means the acid does not penetrate deeply into the formation before it is spent. Mud acids effectiveness is therefore limited in treatments where deep acid penetration is required. There has been recognition for the need to delay the rate of reaction of the acid and consequently a variety of techniques have been developed.

Conventional mud acids would undergo three reactions with sandstone formations: primary, secondary, and tertiary reactions.

Primary reaction

$$19HF + MAlSi_3O_8 + 3HCl \rightarrow \mathbf{3H_2SiF_6} + \mathbf{AlF_2^+} + M^+ + 8H_2O + 3Cl^-$$

Secondary reaction

$$H_2SiF_6 + 6MAlSi_3O_8 + 18HCl \rightarrow \mathbf{6AlF_2^+} + 6M^+ + 18H_2SiO_3 + \mathbf{SiO_2.2H_2O} \downarrow + 18Cl^-$$

Tertiary reaction

$$AlF_2^+ + MAlSi_3O_8 + 4HCl + 4H_2O \rightarrow K^+ + \mathbf{2AlF_2^+} + \mathbf{3H_4SiO_2} \downarrow$$

From the reactions shown, HF is spent quickly and is not regenerated and is unavailable to acidize silicates and silica deep in the formation.

1.5 RETARDED ACIDS

Several methods/additives have been developed to slow down the rate of chemical reaction enabling deeper penetration of the acid. The majors being gelled acids, emulsified acids, organic acids and chemically retarded acids. Gelled acids increase acid penetration by increasing acid viscosity, however these acids are limited to low temperature formations and increased acid viscosity unnecessarily prolongs treatment. Emulsified acids were one of the earliest retarders developed, oil-external emulsified acids are limited by increased frictional resistance. Organic acids have their greatest disadvantage in their cost. Chemically retarded acids although advantageous, become ineffective at high temperatures and pressures.

Recently, three major acid retarders have been identified;

- Boric acid
- Phosphonic acid
- Aluminum chloride

These are based on the addition of compounds containing trivalent metals to HF which affect the reactivity of HF in specific ways. These systems have special mechanisms for delaying HF reaction with silicates and silicas.

1.6 ALUMINUM CHLORIDE

Aluminum chloride ($AlCl_3$) is a white low melting and boiling point solid. $AlCl_3$ has a high affinity for water and forms $AlCl_3.6H_2O$. $AlCl_3$ in its anhydrous form reacts vigorously with bases and water. Precaution should be taken while handling because it causes irritation to the respiratory system, eyes and skin if inhaled or contacted.

Aluminum chloride slows down the reaction and enables deeper penetration into the formation. Aluminum chloride reacts with HF to form aluminum fluoride species. As HF is used up/ spent, the equilibrium of the reaction shifts, thereby allowing the production of more HF. This process has the ability of delaying the production of HF, consequently allowing the live acid to penetrate deeper into the formation and also reducing deconsolidation that might occur. The reaction of HF with $AlCl_3$ is shown below.

$AlCl_3 + 4HF + H_2O \leftrightarrow AlF_4^- + 3HCl + H_3O^+$

As HF spends on siliceous minerals, AlF_4^- hydrolyzes to regenerate HF.

$AlF_4^- + 3H_3O^+ \leftrightarrow AlF^{2+} + 3HF + 3H_2O$

(Nasr-El-Din et al. 2007)

Current research is focused on the determination of the effectiveness of using a retarded mud acid system based on aluminum chloride to acidize sandstone formations compared to conventional mud acids using data from: coreflood analysis and inductively coupled plasma (ICP).

This would involve working on data from several sandstone core samples, using varying temperatures and retarded acid concentrations to thoroughly understand the reactions between HF and alumino silicates.

CHAPTER II

LITERATURE REVIEW

2.1 HISTORY OF ACIDIZING

Acid stimulation of oil reservoirs has been applied since the late 19th century, starting between 1895 and 1896 with Herman Frasch of Standard Petroleum, who was the first to use hydrochloric acid to stimulate carbonate formations. The first acidizing jobs were done by dumping or bailing the acid into place and allowing it to sit until it had its work done and then eventually removed from the well as production fluids were produced. Frasch was also the first to anticipate the need for a postflush in his statement; "It is advantageous to displace the acid and cause it to penetrate further into the rock by forcing a neutral or cheap fluid, such as water into the well".

Over the next 30years there was no recorded history of acidizing until 1928 when Gypsy Oil Co. with the help of Dr Blain Wescott removed calcareous scale from some producing wells. This was also the first time there was any mention of acid inhibitors as Dr. Wescott recommended it to Gypsy Oil Co. but was turned down.

The modern acidizing era started in 1932 with W.A. Thomas of Pure Oil Co. and John Grebe of Dow Chemical Co. They acidizing a dead well with 500gallons of hydrochloric acid which after a brief shut in proceeded to produce 16B/D of oil along with some other wells which were acidized with an inhibited HCl.

2.2 SANDSTONE ACIDIZING

In the 1930s' attempts were made to improve sandstone reservoir production by injecting mixtures of HCl and HF. Starting with Jesse Russell Wilson of Standard oil who patented the application of HF to treat sandstone formation. He recognized the ability of HF acid to react with sandstone and siliceous materials. Wilson B-24 belonging to King Royalty Co. was the first well recorded to have been acidized by HF. It was 1532ft deep with an 11ft producing section. The results after acidizing were disappointing due to the dissolution of the calcareous matrix and the resulting unconsolidated sand which was produced. According to observers, "The reaction products of the acids on the sand seemed to have a plugging effect on the permeability of the formation".

In-situ generation of hydrofluoric acid was also experimented, using sodium fluoride and reacting it with hydrochloric acid. This approach was eventually found to have very damaging effects on the formation due to the presence of sodium salt.

There wasn't much reported success with these early treatments and the HCl/HF mixture was relegated to those wells in which reduced PI was brought about by drilling mud damage. Hence the name now conventionally used, "mud acid." The first treatments were in the Gulf Coast and were sufficiently successful that it became more widely used and garnered interest from the industry.

McLeod in 1984 presented and documented basic guidelines utilized for the proper design of acid treatments based chiefly on formation mineralogy, which is a very important consideration for any acid treatment as acid-formation interaction/ compatibility is very crucial to the success or failure of any acid job. In addition to mineralogy McLeod's guidelines also considers rock permeability. McLeod's table is presented in Table 2.1.

Indiscriminate use of these guidelines can be very detrimental and may cause severe effect to the formation. The guidelines are meant as a starting point for sandstone acidizing and are not all encompassing and have since been modified to address gaps.

Table 2.1 McLeod's guidelines

Formation	**Main acid**	**Preflush**
Solubility in HCl > 20%	Use HCl only	
High Permeability (> 100mD)		
High quartz (> 80%); low clay (<5%)	12% HCl – 3% HF	15% HCl
High feldspar (> 20%)	13.5% HCl – 1.5% HF	15% HCl
High clay (> 10%)	6.5% HCl – 1% HF	Sequestered 5% HCl
High iron chlorite clay	3% HCl – 0.5% HF	Sequestered 5% HCl
Low Permeability (10mD or less)		
Low clay (< 5%)	6% HCl – 1.5% HF	7.5% HCl or 10% Hac
High chlorite	3% HCl – 0.5% HF	%% Hac

(McLeod, 1984)

Kalfayan and Metcalf in 2000 presented a modification of these guidelines using case studies from North America, South America and the Far East. Kalfayan and Metcalf's treatments were based on a diagnosis of formation damage contributors, an in depth evaluation of production and stimulation histories, and a philosophy of production of flexibility and continuous improvement in stimulation procedure and execution practices. (Kalfayan and Metcalf 2000)

Kalfayan and Metcalf's modification based on McLeod's work and he's personal experience is summarized in Table 2.2

Table 2.2 Kalfayan's guidelines

Formation	**Main acid**	**Preflush**
Solubility in HCl > 15-20%	Avoid use of HF	
Calcite or dolomite	15% HCl only	5% NH_4Cl
High iron carbonate (siderite, ankerite)	15% HCl + iron control	5% NH_4Cl + 3% Acetic
High permeability (>100mD)		
High quartz (>80%); low clay (<5%)	12% HCl – 3% HF	15% HCl
Mod. Clay (5-8%); low feldspar (<10%)	7.5 HCl, 1.5% HF	10% HCl
High feldspar (>15%)	13.5% HCl – 1.5% HF	15% HCl
High feldspar (>15%) and clay (>10%)	9% HCl – 1% HF	10% HCl

Table 2.2 continued

Formation	Main acid	Preflush
High iron chlorite clay (>8%)	3% HCl – 0.5% HF or	5% HCl
	10% acetic – 0.5% HF	10% acetic + 5% NH_4Cl
Medium permeability (10-100mD)		
High clay (>5 -7%)	6% HCl – 1% HF	10% HCl
Lower clay (<5 – 7%)	9% HCl – 1% HF	10% HCL
High feldspar (>10 – 15%)	12% HCl – 1.5% HF	10 – 15% HCl
High feldspar (>10 – 15%) and clay (>10%)	9% HCl – 1.5HF	10% HCl
High iron chlorite clay (>8%)	3% HCl – 0.5% HF or	5% HCl
	10% acetic – 0.5% HF	10% acetic + 5% NH_4Cl
High iron carbonate (>5-7%)	9% HCl – 1% HF	5% HCl
K< 25mD	5% HCl-0.5% HF	10% HCl
Low permeability (1-10mD)		
Low clay (<5%); low HCl (<10%)	6% HCl-1.5% HF	5% HCl
High clay (>8-10%)	3% HCl – 0.5% HF	5% HCl
High feldspar (>10%)	9% HCl-1% HF	10% HCl
High iron chlorite clay (>5%)	10% acetic-0.5% HF	10% acetic + 5% NH_4Cl
Very low permeability (<1mD)	Avoid HF acidizing non,	HF matrix simulation
	or hydraulic fracturing is	preferred

2.3 RETARDED ACIDS

Unretarded HF acid (mud acid) reacts so rapidly with siliceous formations that the acid tends to become spent before penetrating deeply into the formation. Consequently, the desired increase in porosity and permeability is limited to areas close to the wellbore while formation damage can extend deeper than regular HF acid systems are able to penetrate.(Gdanski 1985)

Retarded HF (RHF) acids are less reactive with the rock and normally result in deep acid penetration into the formation.(Al-Dahlan et al. 2001) Three retardants mainly used with HF/HCl are; Aluminum chloride, Phosphonic acid, and Boric acid.

Al-Dahlan et al. 2001 investigated these retarded acid systems and concluded that retardation effect is a strong function of temperature and formation mineralogy. He also found that the reaction rate of aluminum chloride retarded mud acid with quartz at 25degC is 50% of regular mud acid and at 75degC it increased to 60%.

Nasr-El-Din et al., 2007 evaluated a new aluminum chloride based acid system with chelating agents at high temperatures – 250 and 300degF and found that at these temperatures, there was a permeability enhancement of the cores and no effect on the integrity of the cores (no produced fines) and also concentration of effluents increased with soaking time (calcium, iron, aluminum, silicon, magnesium), but these experiments were conducted at a flow rate of 2cc/min and an initial soaking time of 3hrs.

The effect of iron precipitation was investigated when sandstone formations are acidized with a retarded mud acid system based on aluminum chloride. For retarded HF acid based on $AlCl_3$, aluminum compounds (sodium hexafluoroaluminate) precipitated at all pH values examined, while iron compounds (sodium hexfluoroferrate) precipitated at pH values that depended on initial iron (III) and HF concentrations. (Nasr-El-Din et al. 2002).

Al-Anazi et al. 2000 designed a cost-effective stimulation treatment to remove formation damage from water injectors in a sandstone field in Saudi Arabia to improve well injectivity while maintaining the integrity of the formation. It was found that to enhance stimulation efficiency, sodium and potassium concentrations have to be reduced. To achieve this, a preflush of 5wt% ammonium chloride should be added to the retarded mud acid based on aluminum chloride and also using 15wt% HCl increased the permeability and ultimately productivity from the reservoir.

A retarded mud acid based on aluminum chloride was used to acidize Pardee D-1 well in the Reddel field, Louisiana. The primary causes of formation damage in the Wilcox sand are clay swelling, fines migration, loss of workover fluids and, residue from acid treatments. After the acidizing treatment, production increased two fold from 500Mcf/D to 1000Mcf/D. A total of 9 wells were acidized after the Pardee D-1 well with 8 out of the 9 being successful and production increment ranging from 2 – 4 fold. The AlHF fluid provided the deep penetration of reactive HF while remaining fully compatible with

feldspar and illite throughout the secondary reactions. (III et al. 1996) (Guichard et al. 1996).

When compared with mud and retarded acid, sandstone acid is less corrosive and user friendly (initial pH around 3), it also requires reduced amount of corrosion inhibitors.(Di Lullo and Rae 1996).

CHAPTER III

EQUIPMENT AND MATERIALS

3.1 BEREA SANDSTONE

The oil and gas industry for over 25 years has used Berea sandstone as the standard test core of choice for experimental studies. Berea sandstone is a sedimentary rock composed primarily of quartz and held together by silica with predominantly sand-sized grains Berea sandstone has very good uniform material properties and these rocks have been used by researchers all over the world to perform numerous core flood testing for and oil and gas production characterization in various sandstone reservoirs due to its relatively high porosity, permeability and material properties. Typical Berea sandstone permeability ranges from 50-200md.

3.2 CORE PLUG DESCRIPTION

Berea sandstone blocks are obtained from Korucek industries and cut into core plugs for use in the coreflood setup using potassium chloride brine to prevent destabilization and swelling of the clays present in the rock. Core dimensions are 6inches length and approximately 1.5inch diameter. Fig. 3.1 shows a sandstone block from the quarry and a plug cored to specification. Core specifications are based on the size of the core holder available for use in the experiment. Berea sandstone's petrophysical properties are relatively variable. However, its mineralogical properties are quite homogeneous, except for carbonate content.(Motta and Santos 1999)

Berea sandstone mineralogy has been investigated and is shown in Table 3.1.

Table 3.1 Berea sandstone mineralogy

Mineral	Percentage, %
Quartz	86
Dolomite	1
Calcite	2
Feldspar	3
Kaolinite	5
Illite	1
Chlorite	2

(Mahmoud et al. 2011)

Fig. 3.1 Berea sandstone

3.3 COREFLOOD

Coreflood studies are performed to allow fluid injection into reservoir rocks under reservoir conditions – temperature and pressure. These studies will be ultimately used to determine initial and final permeability of a rock and to give an indication of damage or enhancement after a compatible acid/chemical has been pumped through the core. One of the major advantages being that different scenarios for chemical flooding can be tried before actually acidizing a real – life well.

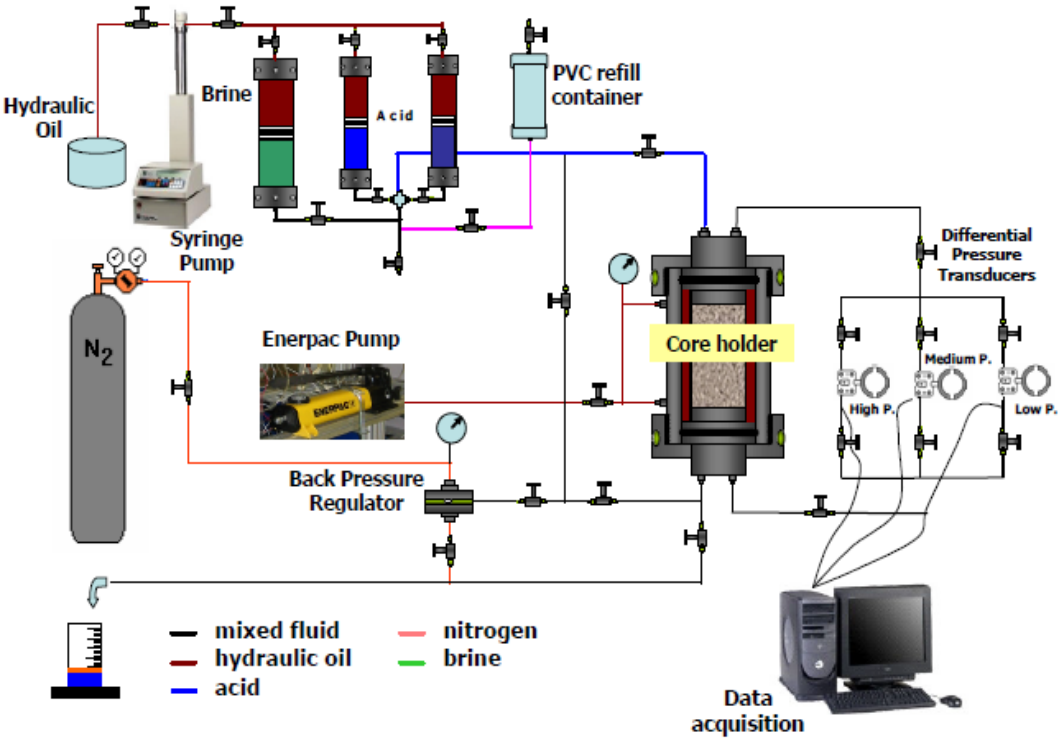

Fig. 3.2 Coreflood setup

Previously prepared brine and acids are put into the accumulators as shown and fluid levels adjusted using the syringe pump and nitrogen gas to increase and reduce levels.

The core is confined inside the core holder using a Viton sleeve and the hydraulic – Enerpac pump. Back pressure is applied to the system to simulate reservoir conditions using nitrogen gas and a Teflon diaphragm BPR to keep CO_2 in solution. Acid is pumped through the core at a constant flow rate under high temperature and pressure and effluent samples are collected at intervals. The spent acid/ effluents are collated at the end of the experiment for further analysis.

During acidizing, the temperature, overburden pressure, back pressure and flow rate are set and maintained constant and the differential pressure across the core as the experiment proceeds is measured by an analog pressure transducer and recorded by the LABVIEW software which would ultimately be used to determine rock response to the acid and determine permeability enhancement or reduction. The experiment is conducted inside a fume hood to vent acid fumes which may be generated as the experiment proceeds. Fig. 3.2 shows a schematic of the major components of the coreflood setup.

The main components of the coreflood setup and their uses are shown in Table 3.2.

Table 3.2 Coreflood components

Component	System requirement
Pump	Capable to work at high pressures, displace a broad range of flow rates and work on either constant flow or constant pressure setting.

Table 3.2 continued

Component	System requirement
Data acquisition system	Collecting, saving and monitoring data generated during the experiment for further analysis.
Accumulators	Constructed with varying special alloys to withstand acid corrosion and to store the acid mixtures and brine solutions required during the different tests.
Temperature regulator	Ability to increase and maintain temperatures to simulate field conditions during experiment.
Back pressure regulator	Capable of providing the necessary back pressure against the flow and keeping generated CO2 in solution. Pressure must be kept constant and preferably 400-500 psi less than overburden pressure.
Core holder	Capable of preventing acid corrosion at high temperatures and pressures and maintain the confining pressure.
Hydraulic pump	Ability to provide and maintain the necessary overburden/ confining pressure to the core in the core holder.
Flow system	Ability to withstand corrosion and to serve as a network for the different fluids – acids and brine to be used in the experiment.

3.4 INDUCTIVELY COUPLED PLASMA

Inductively coupled plasma mass spectrometry is a type of highly sensitive mass spectrometry which has the capability to determine the concentration of a wide range of metals and non-metals at concentrations below one part per trillion. The ICP is a very effective method for trace elemental analysis with its major advantages being; high speed, precision, extreme sensitivity and its ability to scan for multiple elements simultaneously. The ICP functions by putting together a method of ionization and producing ions – inductively coupled plasma and a method of separating and detecting the ions – mass spectrometer. The inductively coupled plasma allows the determination of elements with atomic mass ranging from 7 to 250 which covers lithium to uranium.

The inductively coupled plasma is sustained in a torch which consists of three concentric tubes made mostly of quartz. Argon gas is introduced to induce an electric spark which is applied briefly and in turn introduces free electrons into the gas stream. The plasma used is made by partially ionizing argon gas.

$$Ar \rightarrow Ar^{+} + e^{-}$$

After a sample has been injected into the ICP for analysis, the sample undergoes atomization which is the separation of the sample into individual atoms due to the plasmas extreme temperature, and then the plasma ionizes the atoms which enable them to be detected by the mass spectrometer. Which is of the form;

$$M \rightarrow M^{+} + e^{-}$$

Major components of the ICP are shown in Table 3.3.

Table 3.3 ICP components

Component	Application
Plasma	Ultimately enable determination or metal or non-metal concentration
Argon	Forming and maintaining and plasma, constant flow is required for entire duration of experiment.
Internal standard	Serves as a diluents and consists primarily of de-ionized water
Nebulizer	Converts liquids into an aerosol which can be swept into the plasma to create the ions
Exhaust	Vent high temperatures generated during the experiment
Data acquisition center	Collecting all the data/ concentrations determined during experiment, also used to display analyzed blank and standards before the start of the experiment.
Standard	Injected into the ICP to initiate type of metal or nonmetal concentration to be determined
Sample	Diluted liquid containing ions or metals whose concentrations are to be measured.

3.5 PH METER

A pH meter is an electronic instrument for measuring the alkalinity or acidity – pH of a liquid. A pH meter consists of a measuring probe and an electronic meter which would display the pH reading.

- Probe – The probe measures the pH of a liquid at its glass bulb tip as activity of the hydrogen cations surrounding it. A small voltage is produced which is measured and displays as a pH reading on the connected meter.
- Meter – The meter is a voltmeter which displays in pH units instead of the conventional volts.

An acidic liquid would display a pH range of 1-6, a basic liquid would display a pH of 8-14 and a neutral liquid would display a pH value of 7. Fig. 3.3 shows the major components of the pH meter.

Fig. 3.3 pH meter

3.6 TITRATION

To determine the concentration of an acid or a base, an acid-base titration is utilized. This functions by neutralizing the acid and/or base with an acid or base of known concentration which enables the quantitative analysis of the concentration of a base or acid which is not known. The working principle being the utilization of the neutralization reaction which occurs between acids and bases, and if the exact formulas of these were known, how they would work.

Acid–base titrations can also be used to find percent purity of chemicals.

CHAPTER IV

EXPERIMENTAL PROCEDURE

4.1 REACTION OF MUD ACIDS WITH CLAY

To determine the reactivity of various clays with conventional mud acids, an experiment was conducted by dissolving various clays commonly encountered in oil and gas sandstone reservoirs with;

- Regular mud acid which is composed of 15wt% HCl and 3wt%HF
- Half regular mud acid which is composed of 7.5wt%HCl and 1.5wt%HF

4.1.1 MUD ACID PREPARATION

Regular mud acid (12wt% HCl + 3wt% HF) and half regular mud acid (7.5wt% HCl + 1.5wt% HF) were prepared in the laboratory following the steps;

1. Concentrated HCl was obtained from Mallinckrodt Chemicals
2. Ammonium hydrogen fluoride was obtained from Alfa Aesar Laboratory
3. HCl concentration was determined by titration using NaOH solution.
4. Concentration was found to be 36.34%
5. An excel spread sheet was developed to calculate the required amount of acid in grams for the different acid concentrations
6. Equipment used for acid preparation include;
    - Pipette
    - Beakers
    - Weighing balance

- Stirrer

7. All equipment used in the acid preparation are plastic, as HF reacts with glass ware.
8. The required amount of water is pipette into a beaker
9. Ammonium hydrogen fluoride is added to the beaker and stirred
10. Finally hydrochloric acid is added to the beaker and stirred to ensure proper mixing of the acid.

Final weight composition for the RMHF and HRMHF are shown in Table 4.1

Table 4.1 RMHF and HRMHF

	RMHF (grams)	HRMHF (grams)
HCl	19.49	12.06
H_2O	27.85	36.76
NH_4HF_2	2.661	1.182

4.1.2 REACTION OF CLAY WITH MUD ACID

For this experiment the most frequently encountered clays in the oil and gas industry were used and shown in Table 4.2.

Table 4.2 Chemical formula of clays

Clay	Chemical formula
Kaolinite	A $l_2Si_2O_5(OH)_4$

Table 4.2 continued

Clay	Chemical formula
Chlorite	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2 \cdot (Mg,Fe)_3(OH)_6$
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Montmorillonite	$(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$

The procedure listed below was followed to demonstrate the effect of mud acids on various clays;

1. Kaolinite, montmorillonite, chlorite, and illite were obtained from Wards natural science.
2. Chlorite and illite were supplied as solid rocks and were ground to fine grains with a ceramic mortar and pestle to prevent iron contamination and enable reactivity.
3. Particle sizes of all clay used was determined using a sonic sifter and a microscope.
4. 5 grams each of the different types of clay was mixed with 50 grams each of RMHF and HRMHF (1:10), stirred with a magnetic stirrer for 1hr and left for 24hrs at room temperature.
5. Each mixture was passed through 3.5inch diameter fann filter papers until spent acid and clay are fully separated.
6. To ensure proper separation, retentate was washed with 2litres of water.

7. The retentate obtained in all cases was left to air dry for 48hrs, separated from the filter paper and dried in an oven at 212ºF until completely moisture free.
8. Weight of dry solid was taken using a mass balance to determine losses.

4.1.3 GRAIN SIZE DISTRIBUTION

To determine the grain size of the clay used in the experiment, the grain size distribution was determined following the procedure listed below;

Equipment

- Sonic sifter
- Mortar and pestle
- Air source
- Digital balance
- Set of screens of different sizes

Procedure

1. Inspect all the equipment to be used and clean any equipment that has rock samples or other debris left in it.
2. Measure the mass of the rock sample to be used in the experiment.
3. Place the rock sample in the mortar and use the pestle to grind the sample into individual grains. Be sure to fully grind the sample into individual grains, but do not pulverize the sample. As you grind the sample, do not spill any of it from the mortar.

4. Select the first five large meshes sieves. Individually weigh each of the sieves.
5. Stack the selected sieves according to mesh size. The sieve number on the side (for example, 10-325) will aid in determining the order. The largest of the sieve numbers should be on the bottom. Place the sleeves on top of the bottom assembly, which is the stand with latex sides.
6. Apply the spring-loaded top of the assembly and secure the arms to the top of the bottom assembly.
7. Place the entire assembly in the sonic sifter. The spring-loaded top will need to be depressed to fit inside the sifter.
8. Slide the assembly into the sifter and allow the switch on the left side to flip back.
9. Close the door of the sifter.
10. Turn on the power toggle switch.
11. Set both the pulse and sift values to 9.
12. Turn the main time knob to 15 minutes and depress the button next to the number 11 on the same switch.
13. Allow the sifter to run for the allotted 15 minutes.
14. Gently remove the sifter apparatus from the machine. Weigh each individual sieve and note the content. The difference between the empty weight and the weight after sifting is the volume trapped in the sieve.
15. Repeat the above procedure for the second set of sieves with the sample collected in the pan. Discard the sample retained by the larger meshes.

4.2 COREFLOOD

4.2.1 CORE PREPARATION

The core holder available is a 6 in length by 1.5 in diameter core holder, therefore before the experiment the rock is cut and the pore – volume/ porosity is determined to calculate the amount of acid to be injected. The following steps are followed;

1. The core is dried in the oven for atleast 6 hours to ensure it is completely moisture free.
2. Measure dry weight – A
3. Saturate the core overnight with brine – 5wt% NH_4Cl brine
4. Measure the saturated weight – B
5. Determine the density of the fluid using a density meter
6. Calculate the pore volume.

$$Pore\ volume = \frac{(B - A)}{density\ of\ brine}$$

7. Determine the pore volume of acid to be injected for the core flood experiment based on the rocks calculated pore volume.

4.2.2 RETARDED ACID PREPARATION

Following the steps listed in 4.1.1 – mud acid preparation, retarded mud acid is prepared the only addition being 5wt% $AlCl_3$ which acts as the retardant slowing down the rate of the chemical reaction. An excel spread sheet was developed for this a sample shown in Table 4.3 for the retarded mud acid – 1.5wt% HF,15wt% HCl and 5wt% $AlCl_3.6H_2O$.

Table 4.3 Acid calculations

	M, g/mol	Purity, %
HF	20.0064	
NH_4HF_2	57.04	95
HCl	36.4	36.34
$AlCl_3$	133.34	
$AlCl_3$ $6H_2O$	241.43	
Al	26.98	
		units
Total Solution	100	g
Density of $AlCl_3$	1.266	g/cm3
	weight%	
HCl	0.15	
HF	0.015	
$AlCl_3$ $6H_2O$	0.05	
$NH_4HF_2 + HCl = 2HF + NH_4Cl$		
M HF	0.074976	mole
M HCl	0.037488	mole
M NH_4HF_2	0.037488	mole
m NH_4HF_2	**2.250859**	**g**
m HCl	**45.03182**	**g**
C $AlCl_3$ $6H_2O$	3.706449	mol/L
m $AlCl_3$ stock	**7.073827**	**g**

The governing equations to calculate mass of the main components of the retarded mud acid mixture are shown below and are highlighted in Table 4.3 for 100g of solution. The same excel sheet is also used to calculate mass of acids used to prepare regular mud acid.

$$Mass\ of\ NH_4HF_2 = Molar\ mass\ of\ NH_4HF_2 \times \frac{57.04}{95}$$

$$(15wt\% \times 100g) + (Molar\ mass\ of\ HCl \times 36.4) = Mass\ of\ HCl \times 36.34wt\%$$

$$Mass\ of\ AlCl_3 = \frac{\left(\frac{5g \times 26.98}{241.43}\right)}{100 \times 1000 \times 1.266g/cm^3}$$

4.2.3 COREFLOOD PROCEDURE

1. Ensure the core holder is clean and free of solids before the experiment starts to maintain a constant pressure and prevent leakage during the experiment.
2. Put the core inside the core holder and properly close the inlet and outlet.
3. Refill the hydraulic pump to ensure enough oil to complete the experiment or last at least 6hrs.
4. Clean the accumulators by rinsing them with fresh water.
5. Fill the accumulators with a pre flush, main acid and post flush in that sequence and pressurize the fluids by running them through the lines to ensure all the air is removed.
6. Check nitrogen cylinder is not empty.
7. Open the nitrogen cylinder; apply a backpressure and an overburden pressure to the set-up. Also apply a safety pressure if using a high temperature.
8. Open the inlet and outlet valves to the core holder and ensure that the pressure relief valves are closed to maintain system pressure.

9. Set the flow rate and run the pump. Once there is a pressure differential across the system there would be flow from the outlet.
10. Start the program LABVIEW to record the pressure drop
11. Calculate the initial permeability of the rock using Darcy's equation.

$$k = \left(\frac{q\mu L}{A\Delta p}\right)$$

where,

k = permeability, md

Q = flow rate, cm^3/sec

μ = viscosity of the fluid, cP. Measured with a capillary viscometer

L = length of the core, in

A = Area of the core, in^2

ΔP = Pressure drop, psi

12. If using high temperature, ensure it is properly connected and start heating up the system.
13. When steady state is achieved – when pressure drop remains constant, begin flowing acid through the system. Amount of acid injected for all experiments is shown in Table 4.4.

Table 4.4 Injected acid

Acid injected	Pore volume
Pre-flush	2 PV
Main acid	2 PV
Post-flush	4 PV

14. Ensure that a sufficient amount of post flush is used to ensure all the acid is removed from the system.
15. Once the experiment is over, switch of the heater, stop the pump and stop the LABVIEW program – data is automatically saved.
16. Relieve the system pressure by closing the nitrogen gas cylinder and opening the gas outlet slowly.
17. Open all plugs and valves to slowly depressurize the lines.
18. Take out the core with gloves if high temperature is used.
19. Run the pump to displace all the fluid left in the vessels.
20. Refill the accumulators with fresh water and run through the system to ensure all the lines are acid free to prevent corrosion.
21. Ensure the accumulators are empty and clean.
22. Refill and shutdown the pump.
23. When the system has properly cooled down (check temperature using regulator), the final permeability is determined using Darcy's equation.

4.2.4 DATA ACQUISITION

Before the core flooding begins, a file needs to be created in the LABVIEW software where the data during the experiment – pressure drop and time, would be collated and stored for further data analysis. LabView displays are shown in Figs. 4.1 and 4.2. This is created using the procedures listed below.

1. Open Acidizing LabView→ Window→ show block diagram
2. Double click to write a new file (name, location, comments)
3. Ones the file is made, close the block diagram window
4. Go to the front panel and click the run/play icon and begin to collect data
5. Data will be transmitted from the coreflood transducers as long as the experiment is still running.
6. After the experiment, shut down LabView.

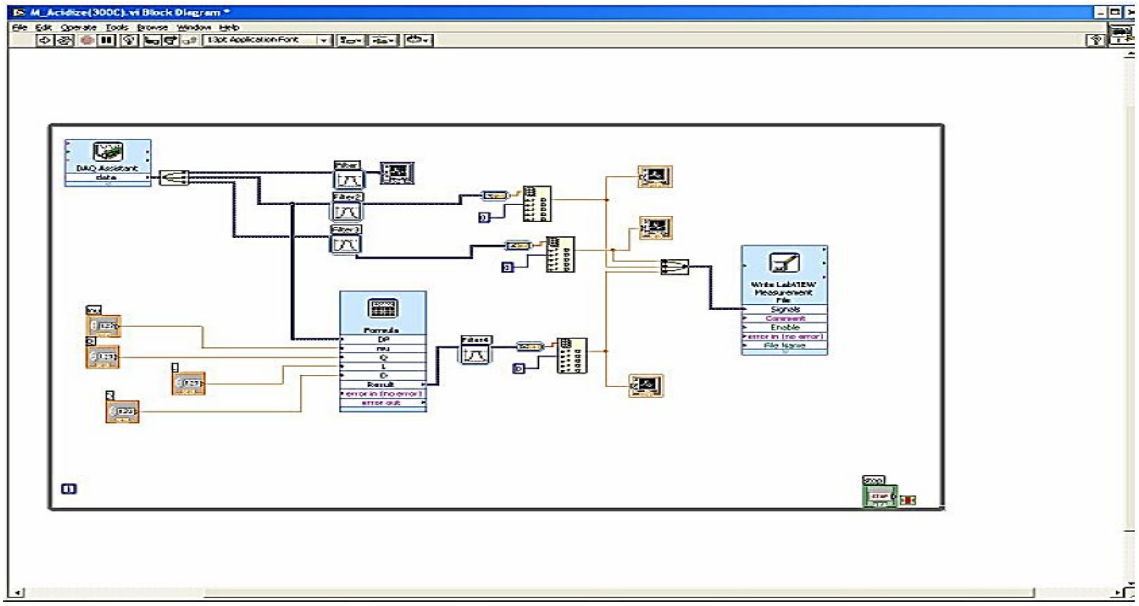

Fig. 4.1 LabView

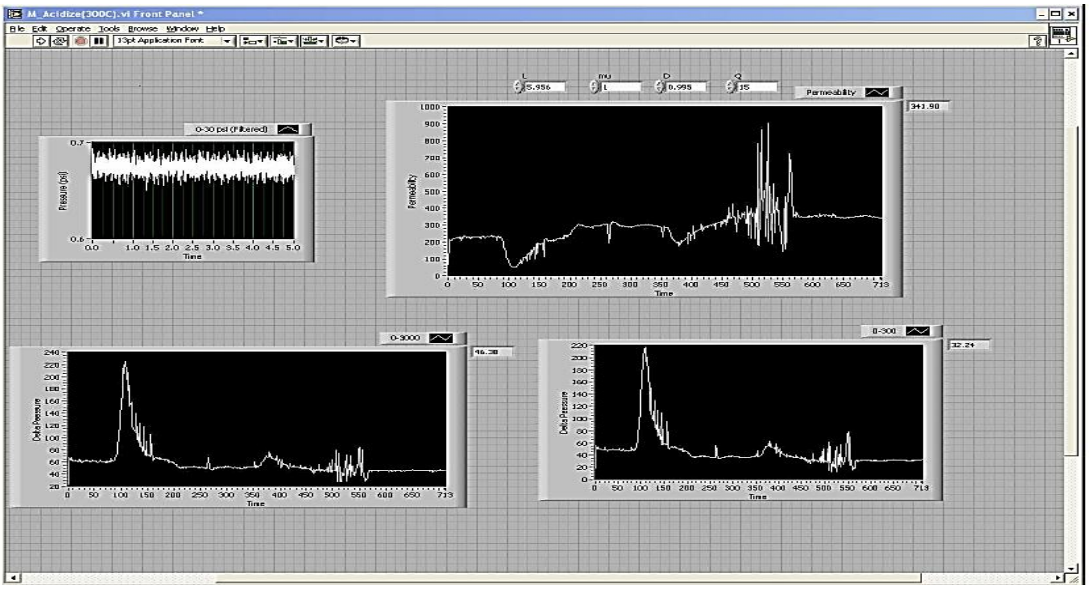

Fig. 4.2 LabView data acquisition

4.2.5 COREFLOOD PARAMETERS

During the coreflood experiment, there are two sets of parameters – changing parameter and constant parameters. Fig. 4.3 shows the coreflood setup used for all the experiments and Table 4.5 shows the key parameters involved.

Table 4.5 Coreflood parameters

Constant parameters	Changing parameters
Flow rate	Differential pressure
Temperature	➢ Measured by transducers
Confining pressure	➢ Recorded by LABVIEW software
Back pressure	

Fig. 4.3 Coreflood setup in lab 720

4.3 DISSOLUTION REACTION

The experiment was carried out to demonstrate the retarded nature of $AlCl_3$. By dissolving similar berea sandstone rocks (1in diameter by 1.5in length) one in a beaker containg retarded mud acid and another in a beaker containing mud acid, the nature of the retarded acid is demonstrated following the procedures listed below;

1. Dry weight of the cores are taken before the start of the experiment
2. Cores are saturated in fresh water for 24hrs and the saturated weight is measured
3. 500ml of regular and retarded mud acid were prepared in separate plastic beakers
4. Using a syringe, 10ml is collected from each of the beakers for further analysis

5. Cores are tied with a string and submerged into beakers of acid
6. Cores are left to saturate for 5minutes after which they are washed, dried, and weighed.
7. A syringe is used to collect 10ml of acid from each beaker after the core is removed.
8. Core is re-saturated and process is repeated 11 more times for a total of 60mins, samples of acid and weights collected at each step.
9. Acid samples collected are further analyzed for mineralogy.
10. Weights of core are collected to determine mass loss and ultimately determine acid reactivity.

4.4 INDUCTIVELY COUPLED PLASMA

Determination of mineralogy using the inductively coupled plasma was conducted following the steps listed below. Fig. 4.4 show the ICP used for experiments.

4.4.1 EQUIPMENT

- Deionized water
- Sample tubes
- Pipette
- Volumetric flask
- Fluids – blank, standard, and sample

4.4.2 PROCEDURE

1. Ensure blank and standard are sufficient. Atleast 5cc for each.
2. Start exhaust fan
3. Check nitrogen cylinder is not empty, start it.
4. Check argon cylinder is not empty, start it.
5. Start air valve.
6. Close the peristaltic pump clamps.
7. Start ICP – OES.
8. Start software WinLab32.
9. Click on plasma icon. Start pump.
10. Wait till bubbles are seen in sample tubing and then ignite plasma.
11. Allow plasma to stabilize for 30 – 40 min. Let it automatically initialize optics.
12. Once initialization value is seen in display, select method.
13. Open calibration, results and manual windows.
14. Analyze the blank.
15. Analyze the standard. Observe the spectra and check the wavelengths.
16. Analyze the samples.
17. Select utilities – data manager – print report.
18. Turn plasma off and wait for gases to purge.
19. Turn off all cylinders and air valve.
20. Turn WinLab32 off.
21. Turn ICP – OES off.

22. Release tension in the tubings.

23. Finally turn the exhaust off.

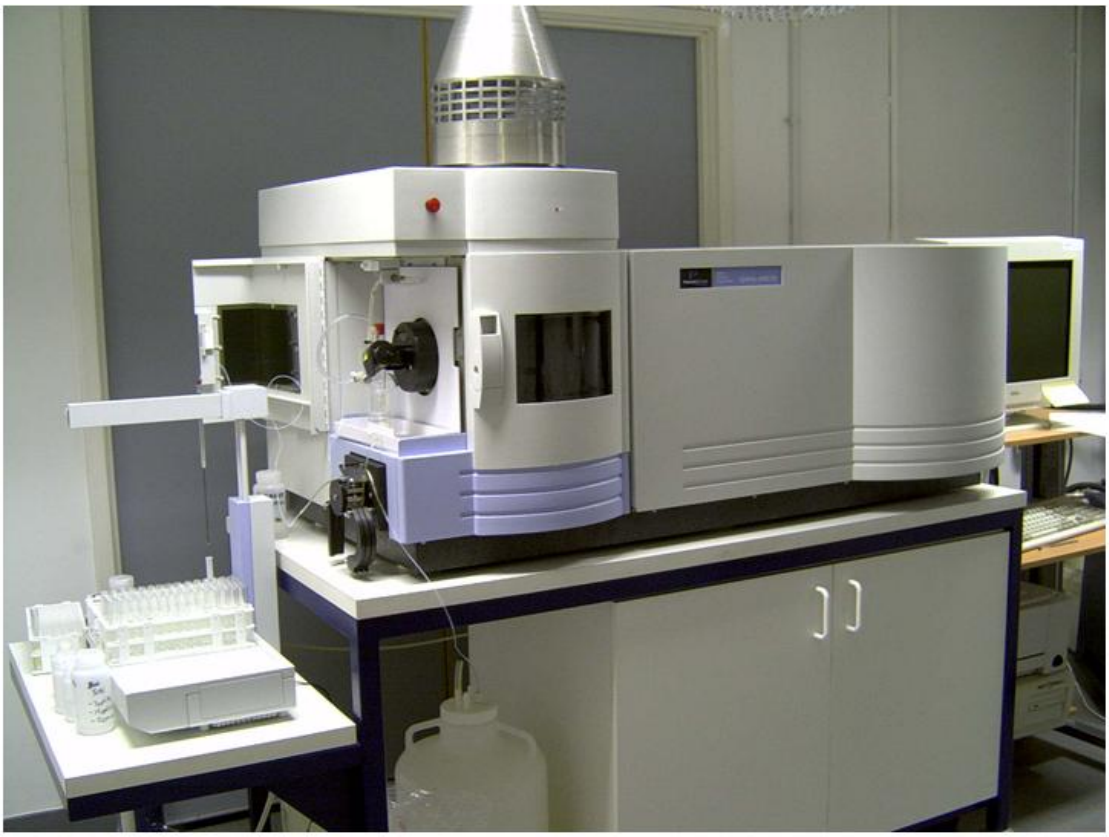

Fig. 4.4 Inductively coupled plasma (ICP)

4.5 ACID – BASE TITRATION

To determine acid concentration in effeluent samples from core flood analysis, acid – base titration was carried out follwing the steps listed below.

1. Prepare the base – sodium hydroxide (NaOH). 0.2M NaOH was used.
2. Put the base solution into appropraite flask on the equipment.

3. Remove the probe from the storage solution.
4. Rinse with deionized water and wipe dry with a lint free cloth.
5. Calibrate probe with atleat 2 standards.
6. Check that slope is in the range 95 – 105.
7. Displace atleast 30ml of base to ensure air bubbles are absent from tubing.
8. Pipette 1ml of sample into a plastic beaker and fill up with atleast 50ml of deionized water.
9. Insert titration assembly into the fluid, ensuring that all three components are properly inserted.
10. Check that the pH is lower than 6 to ensure acidity of the solution.
11. Choose method and begin titration.
12. Amount of base injected would display after the end point is reached which is used to calculate acid concentration.
13. Between test samples, probe is cleaned with deionized water to prevent contamination.
14. After experiment is completed, properly clean probe and place in storage solution.

$$\boldsymbol{Concentration\ of\ acid,\ {}^{mol}/_{l}} = \frac{Volume\ dispensed\ \times Concentration\ of\ base}{Volume\ of\ sample\ added}$$

Chemical equation for the titration;

$$HCl + NaOH \rightarrow NaCl + H_2O$$

CHAPTER V

RESULTS AND DISCUSSION

5.1 REACTION OF MUD ACID WITH CLAYS

5.1.1 MASS READINGS

Mass readings were taken for spent clay to determine percentage weight loss for 5g each of clay. Results obtained are shown in Table 5.1, and weight losses in Figs. 5.1 and 5.2.

Table 5.1 Weight loss of clays

Mixture	Mass of sample after experiment
RMHF + kaolinite	56.13%
HRMHF + kaolinite	47.20%
RMHF + montmorillonite	37.64%
HRMHF + montmorillonite	27.91%
RMHF + chlorite	79.82%
HRMHF + chlorite	48.51%
RMHF + illite	59.71%
HRMHF + illite	39.99%

Fig. 5.1 Dissolved clay

Figure 5.1 shows acid quickly dissolving chlorite after the clay was put into the acid mixture.

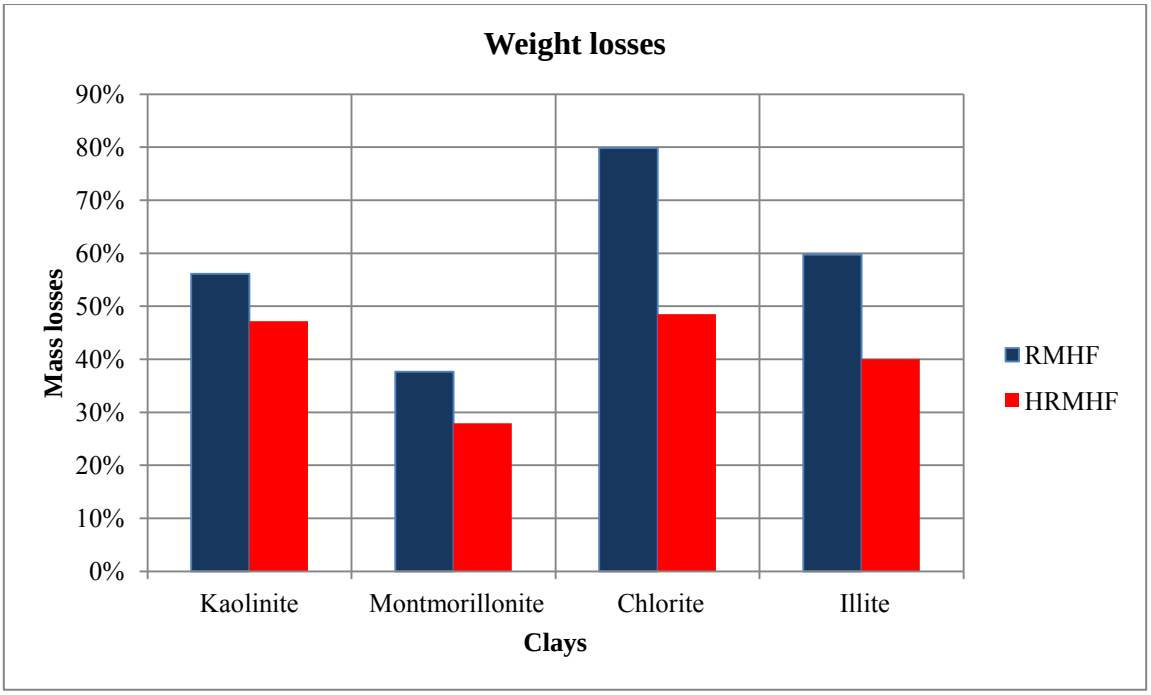

Fig. 5.2 Weight loss of clays

5.1.2 GRAIN SIZE DISTRIBUTION

The grain size distribution after the rocks were crushed and analyzed with the sonic sifter is shown below.

Montmorillonite and kaolinite; 62 – 88 μ

Illite and Chlorite; 62 – 125 μ

For the experiment, only grain sizes ≤ 62 μ were used.

5.1.3 pH

Tables 5.2 and 5.3 shown below show the pH of the spent acid filtrate after the reaction of the different clays with mud acid and the pH of freshly prepared acids.

Table 5.2 pH of spent acid

Spent Mud acid filtrate	Kaolinite	Illite	Montmorillonite	Chlorite
RMHF	0.00	0.00	0.00	0.00
HRMHF	0.12	0.08	0.11	0.13

Table 5.3 pH of fresh acid

Mud acid	pH
RMHF	1.62
HRMHF	1.47

5.1.4 COLOR

For the spent acid, a consistent color disparity was noticed between the RMHF and HRMHF. The filtrate of the regular mud acid was always darker than the half regular mud acid for all the clay sample formations tested. Fig. 5.3 shows various colors of clay.

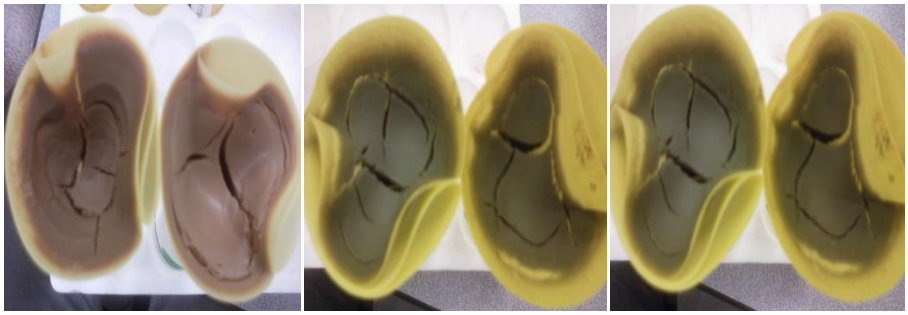

Fig. 5.3 Samples of the spent clay

5.1.5 ANALYSIS OF FILTRATE

Chemical composition of the spent acid was investigated using the inductively coupled plasma to determine the concentration of the key ions. Table 5.4 shows the analysis of the filtrate and Fig. 5.4 shows a bar chart of the analysis with the different clay additives.

Table 5.4 Analysis of filtrate

	Aluminum, mg/l	Silicon, mg/l	Iron, mg/l
RMHF+K	9479	4748	605
HRMHF+K	6572	1120	537
RMHF+M	1851	4813	1135

Table 5.4 continued

	Aluminum, mg/l	Silicon, mg/l	Iron, mg/l
HRMHF+M	4082	5708	1987
RMHF+I	529	1707	994
HRMHF+I	934	2340	1582
RMHF+C	1886	2560	2793
HRMHF+C	1288	913	1597

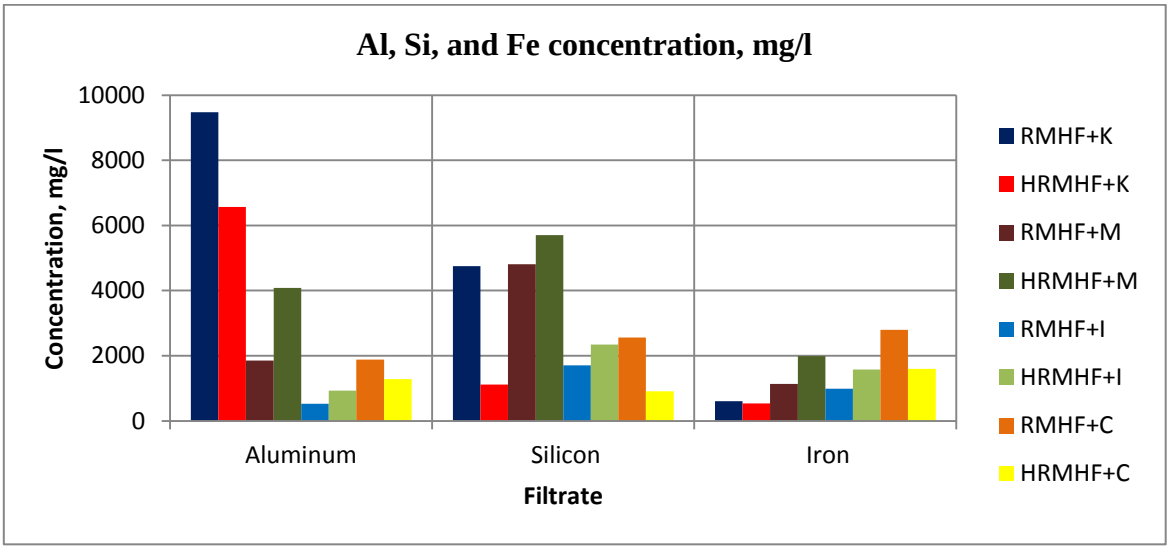

Fig. 5.4 Analysis of filtrate

5.1.6 DISCUSSION

Based on the work done with clays, the following were observed and can be concluded;

1. A considerable amount of clay was lost in the reaction with mud acid. As observed, more clay was lost in all cases in the reactions with RMHF than the

reactions with HRMHF due to the greater concentration of acid present.

2. Although still acidic, the pH of the spent mud acid filtrate is significantly lower than the freshly prepared acid. A possible explanation for this is that most or all of the HF in the mud acid has been consumed in the reaction of the clay and HCl is predominately what is left in the spent acid solution.
3. Weight loss was observed in all the clay samples tested as shown in Table 5.1 and Fig. 5.2 indicating that the mud acid is capable of dissolving silicates and silica present in the clay.
4. Weight loss maximum in chlorite and minimum in montmorillonite.
5. Illite when dissolved in acid produced a lot of fines.
6. Constant color consistency observed in spent acid.
7. Mineralogy from ICP show metals present hence appropriate additives needed to keep these metals in solution.

5.2 COREFLOOD RESULTS

5.2.1 COREFLOOD EXPERIMENT 1

Experimental conditions are listed below

Temperature of experiment – room temperature

Pre-flush – 5wt% Ammonium chloride brine

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Post-flush – 5wt% Ammonium chloride brine

Flow rate – 5cc/min

Initial permeability: 63md

Final permeability: 63md

Figs. 5.5 and 5.6 show the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and concentration of key ions from effluent samples from the ICP respectively.

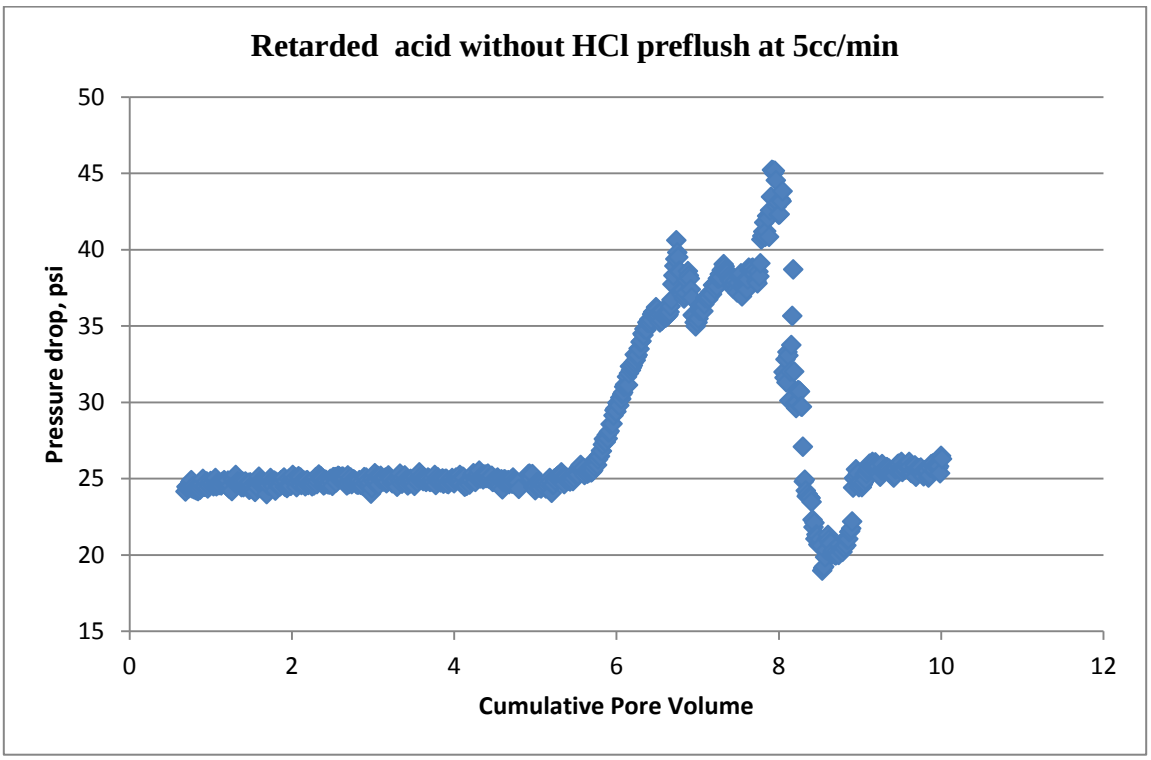

Fig. 5.5 Retarded mud acidizing without HCl preflush at 5cc/min

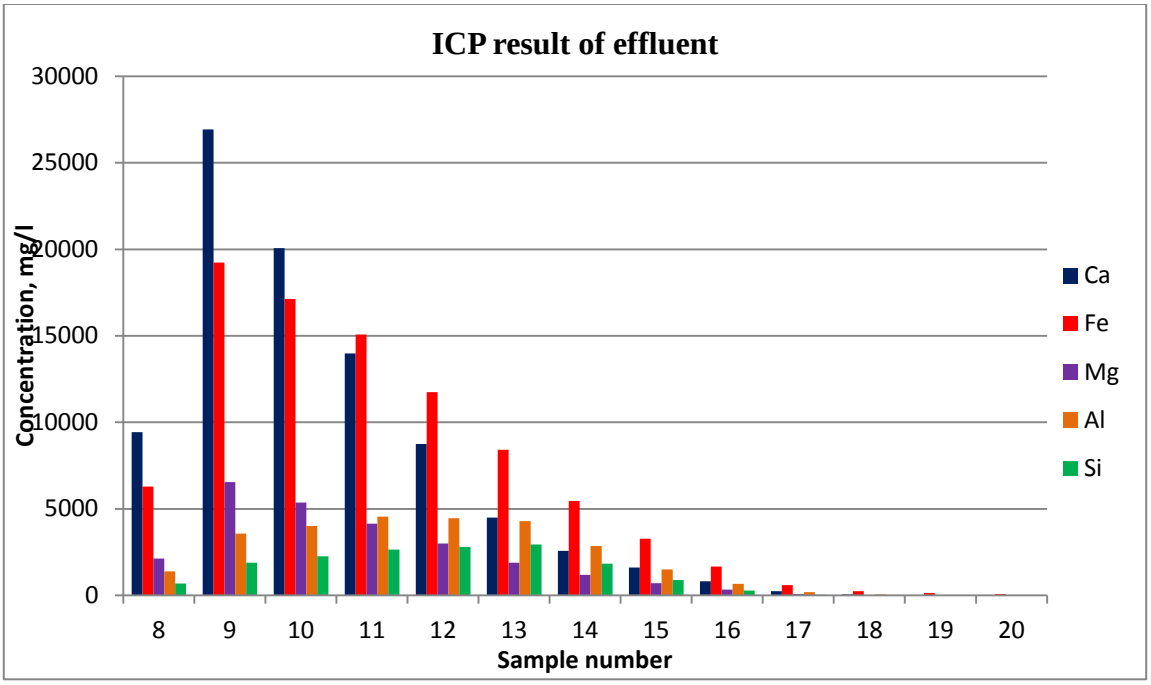

Fig. 5.6 ICP result of effluent experiment 1

Discussion

Based on the work done, the following is observed and understood;

1. Initial and final permeability of the core are the same.
2. After about 8mins of injecting retarded acid, effluent changes color—becomes darker, flow becomes faster and turbulent at the same flow rate and gas bubbles appear.
3. These gas bubbles can be attributed to CO_2 which is evolved as the HCl in the retarded acid reacts with the $CaCO_3$ present in the sandstone rock.

   $CaCO_3\,(s) + 2\,HCl\,(aq) \rightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$

4. Permeability remains the same as a result of formed calcium fluoride as the HF in the mud acid mixture reacts with $CaCO_3$ present in the sandstone rock.

   $CaCO_3 + HF \rightarrow CaF\ (ppt) + HCO_3\ (g)$
5. Retarded nature of acid was very evident in experiment as the permeability wasn't impaired by the formation of CaF.
6. Color of the effluent remains throughout the main acid stage but gradually fades as postflush is carried out and becomes totally clear by the end of the postflush.
7. Sandstone core had changed in color from light brown to a clear very light grey by the end of the experiment.
8. Mineralogy of spent samples indicates that a lot of calcium was evolved during this experiment, hence $CaCO_3$ dissolved.
9. Next experiments will be carried out at elevated temperatures (150degF and 300degF) – all other conditions remaining constant.

5.2.2 COREFLOOD EXPERIMENT 2

Temperature of experiment – 150degF

Preflush – 5wt% Ammonium chloride brine

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 5cc/min

Initial permeability: 65.4md

Final permeability: 45md

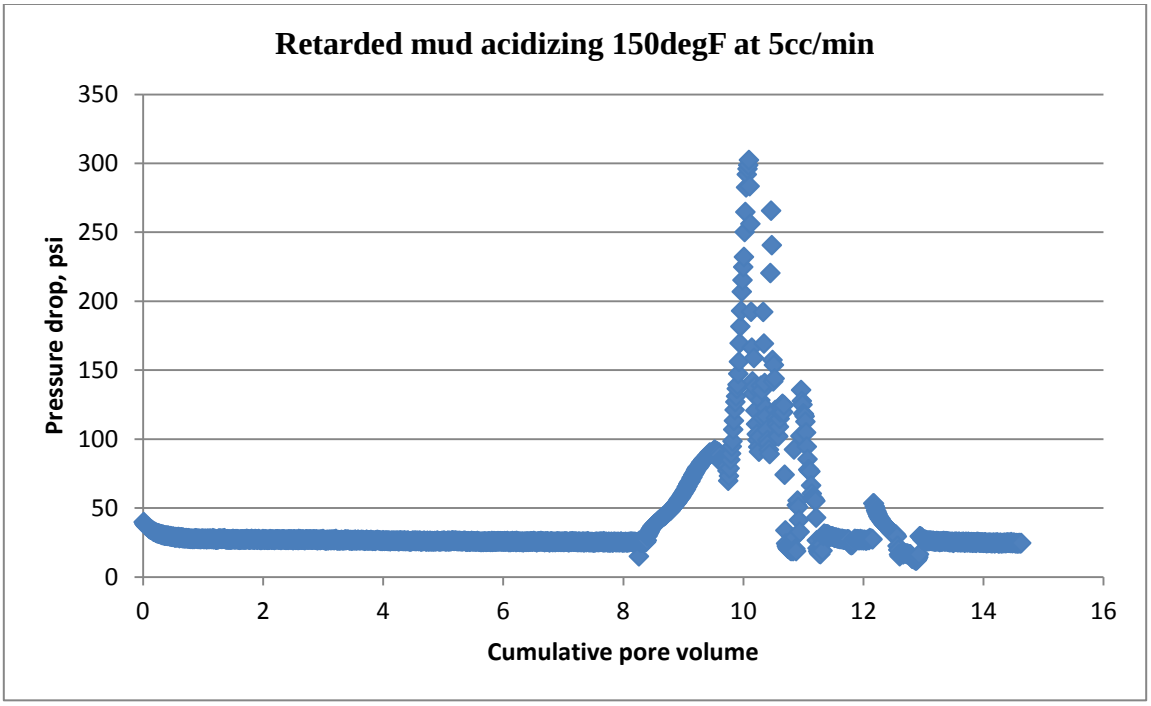

Fig. 5.7 Retarded mud acidizing 150degF at 5cc/min

Table 5.5 Mineralogy of spent retarded acid at 150degF without HCl preflush

Ca	Mg	Fe	Si	Al
0	0	0	0	0
9710	2178	6217	0	168
35090	8981	27620	0	517
5902	2426	12270	0	520
2849	2457	14950	259	6369
1809	3113	16550	1786	10540
1190	1669	8994	3326	8130
869	875	5211	2538	5390
479	288	2268	48	1235
310	83	1129	0	402
0	0	292	0	154

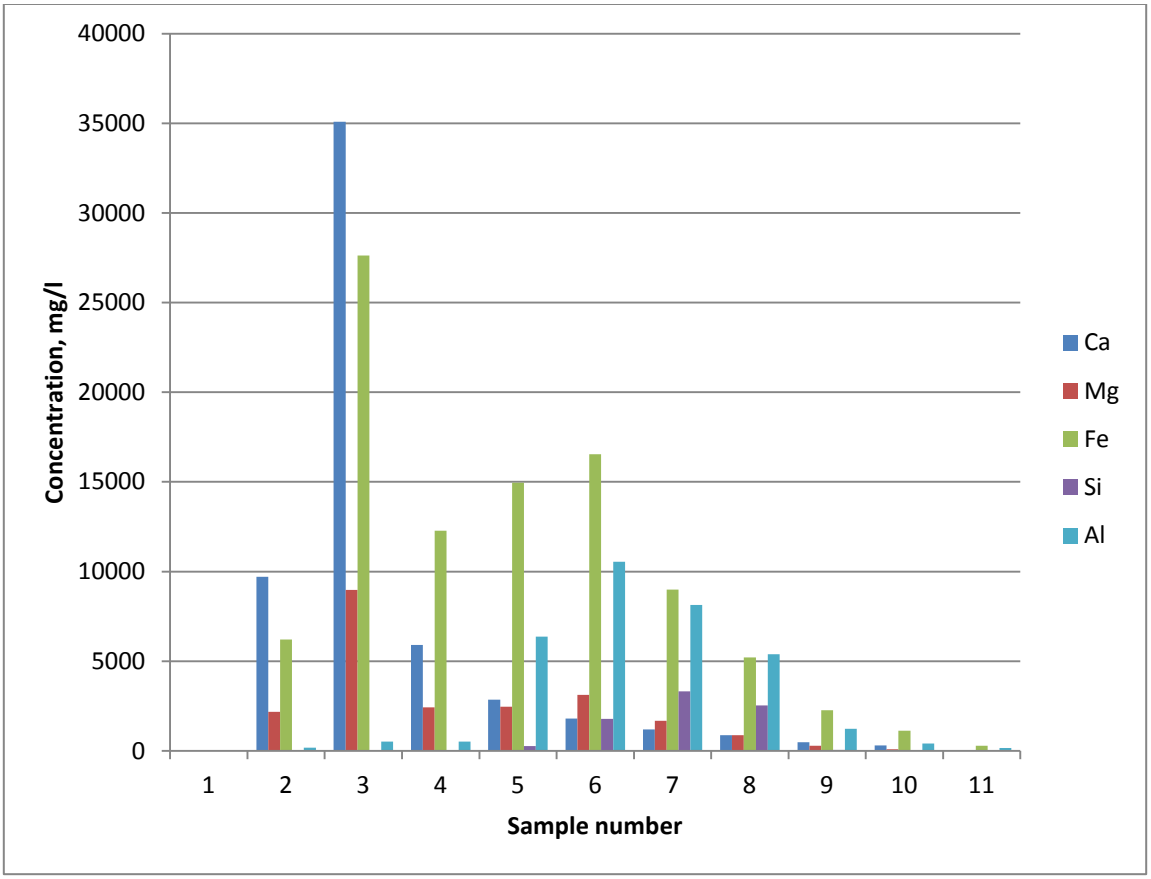

Fig. 5.8 ICP result of effluent experiment 2

Fig. 5.7 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.8 and Table 5.5 show the concentration of key ions from effluent samples from the ICP.

5.2.3 COREFLOOD EXPERIMENT 3

Temperature – 300degF

Preflush – 5wt% Ammonium chloride brine

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 5cc/min

Initial permeability: 65md

Final permeability: 41.2md

Fig. 5.9 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.10 and Table 5.6 show the concentration of key ions from effluent samples from the ICP.

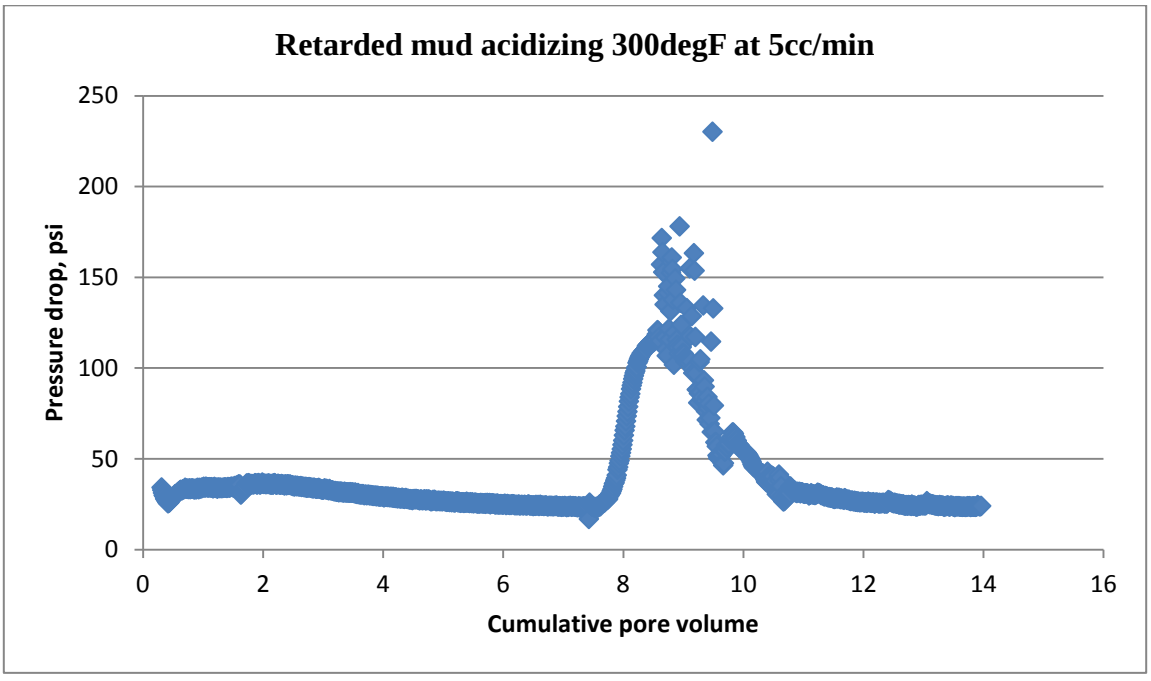

Fig. 5.9 Retarded mud acidizing 300degF at 5cc/min

Table 5.6 Mineralogy of spent retarded acid at 300degF without HCl preflush

Ca	Mg	Fe	Si	Al
0	0	0	0	0
8865	2447	9828	0	425
31150	9457	40890	978	3689
8983	4119	17780	0	3830
3115	2745	11910	0	8370
1533	1156	5310	406	11250
1589	1004	4684	758	14710
1185	627	3300	519	9441
716	232	1545	0	1159
676	143	945	0	439
341	17	516	0	201

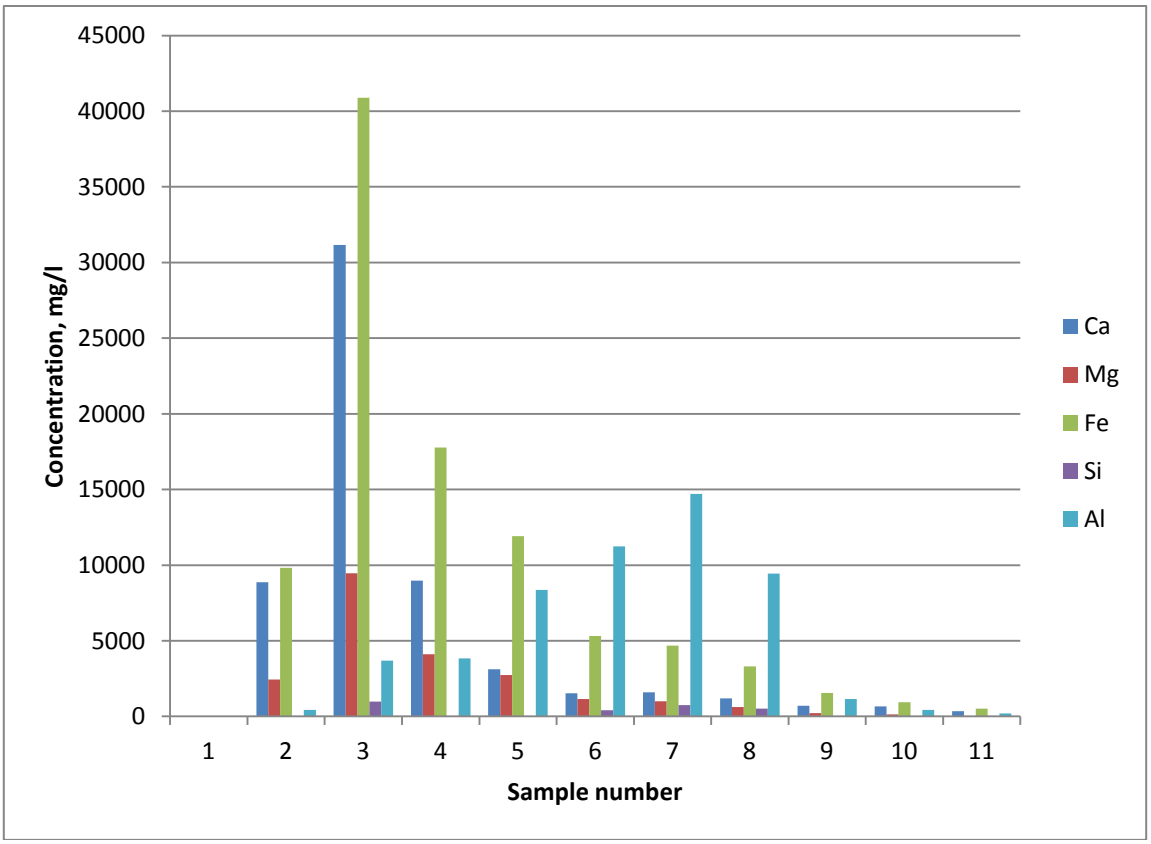

Fig. 5.10 ICP result of effluent experiment 3

Discussion

Based on the work done, the following is observed and understood;

1. Permeability reduction occurred when experiment was performed at elevated temperatures such as would be experienced in an actual oil and gas reservoir. At 150degF, a 31% permeability drop occurred and at 300degF, a 37% permeability drop occurred.
2. When compared to experiment 1 shown in Fig. 5.5, which had the same conditions only variant was the application of a higher temperature but which had no permeability impairment, it can be concluded that higher temperatures would adversely affect the permeability of a sandstone rock due to unwanted precipitations formed at these temperatures.
3. A possible solution to this is to introduce a preflush, such as HCl which would dissolve all unwanted $CaCO_3$ present before the main acid which contains HF is introduced to prevent the formation of CaF which is suspected to have impaired the sandstone rock.
4. A significantly higher amount of calcium if found in effluent for experiments 2 and 3 when compared to experiment 1.
5. High amount of iron found in effluent can be attributed to corrosion in coreflood setup as acid flows through at higher temperatures.
6. A possible solution is to increase the amount of corrosion inhibitor in acid.
7. Next set of experiments are conducted at same experimental conditions, but with the addition of HCl preflush.

5.2.4 COREFLOOD EXPERIMENT 4

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 5cc/min

Initial permeability: 64md

Final permeability: 105md

Fig. 5.11 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.12 and Table 5.7 show the concentration of key ions from effluent samples from the ICP.

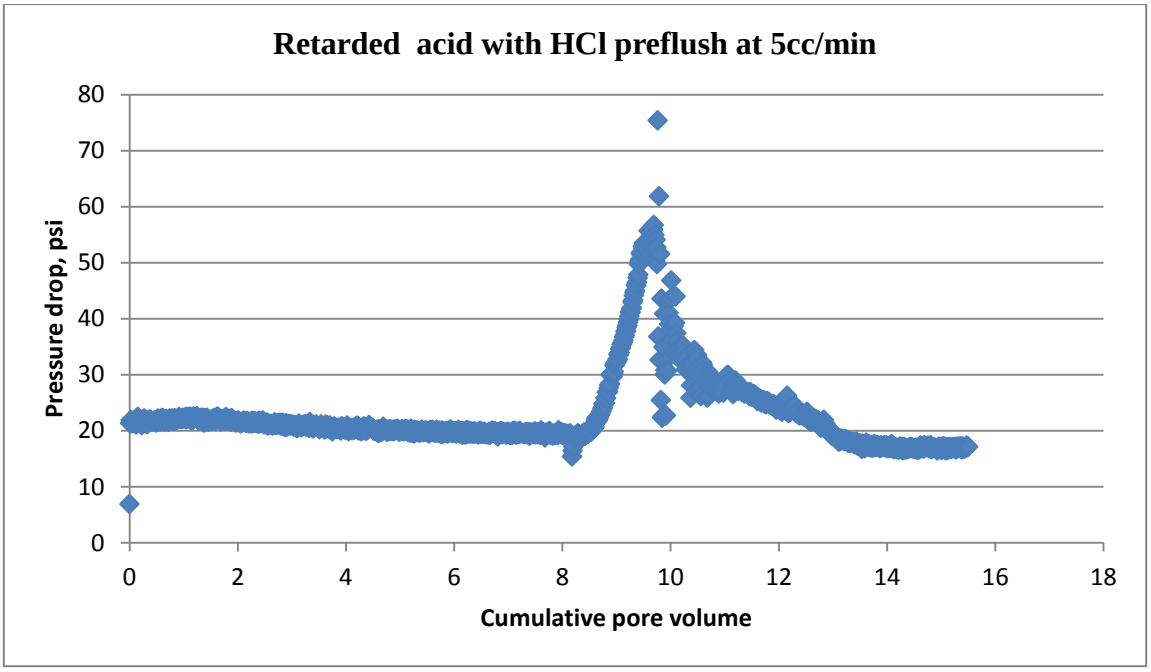

Fig. 5.11 Retarded mud acidizing with HCl preflush at 5cc/min

Table 5.7 Mineralogy of spent retarded acid at 300degF and 5cc/min

Ca	Mg	Fe	Si	Al
8707	1963	8980	32	403
17540	5566	25330	0	2470
4499	2226	12550	0	2874
2653	2820	13640	0	7639
1170	1574	8075	491	11400
796	766	4859	713	11380
572	290	2854	676	8733
0	0	1349	0	1835
0	0	286	0	448
0	0	0	0	231

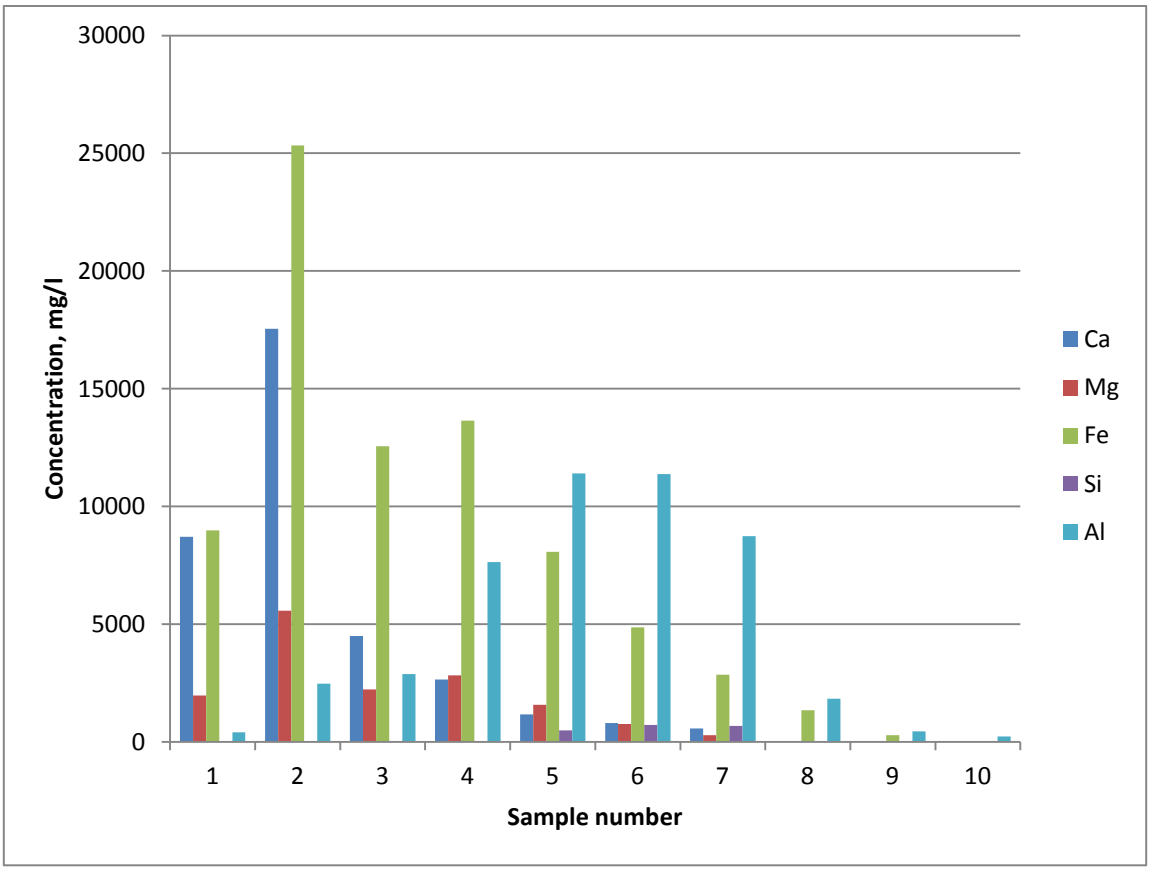

Fig. 5.12 ICP result of effluent experiment 4

5.2.5 COREFLOOD EXPERIMENT 5

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a regular mud acid (1.5wt%HF, 15wt%HCl)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 5cc/min

Initial permeability: 64md

Final permeability: 102.4md

Fig. 5.13 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.14 and Table 5.8 show the concentration of key ions from effluent samples from the ICP.

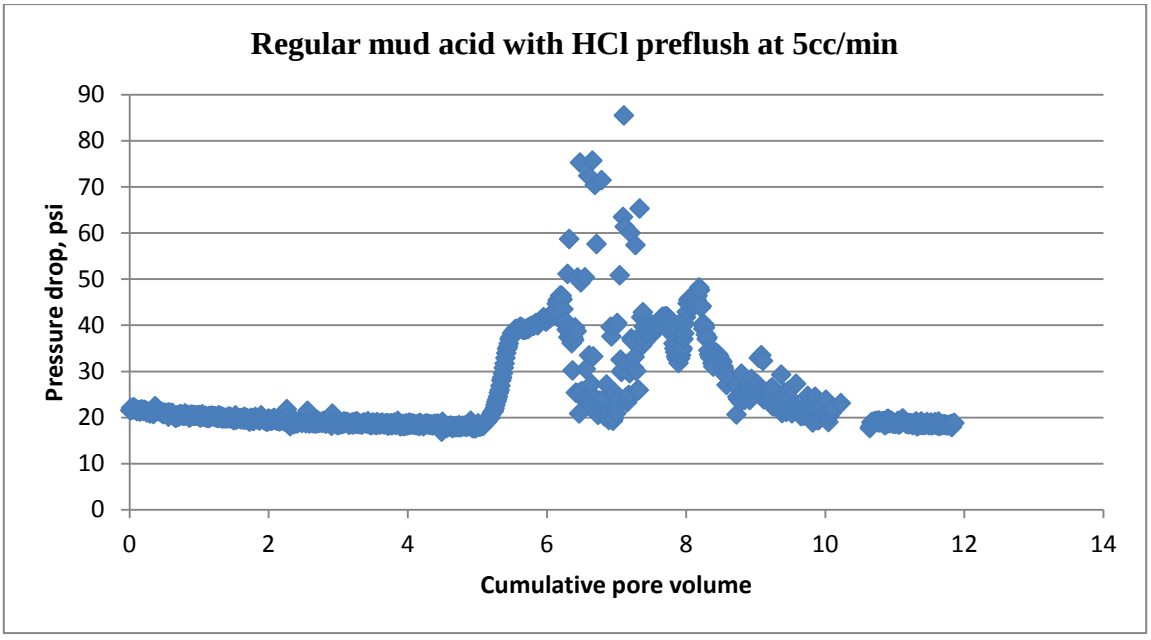

Fig. 5.13 Regular mud acidizing with HCl preflush at 5cc/min

Table 5.8 Mineralogy of spent regular acid at 300degF and 5cc/min

Ca	Mg	Fe	Si	Al
8675	1866	8037	26	436
23200	6899	30570	595	2492
5960	2888	14550	0	2963
2207	2884	14190	317	7944
805	1436	7500	2973	12370
686	827	5163	2556	12820
315	366	3163	1735	9304
114	0	1216	341	1877
0	0	0	0	212

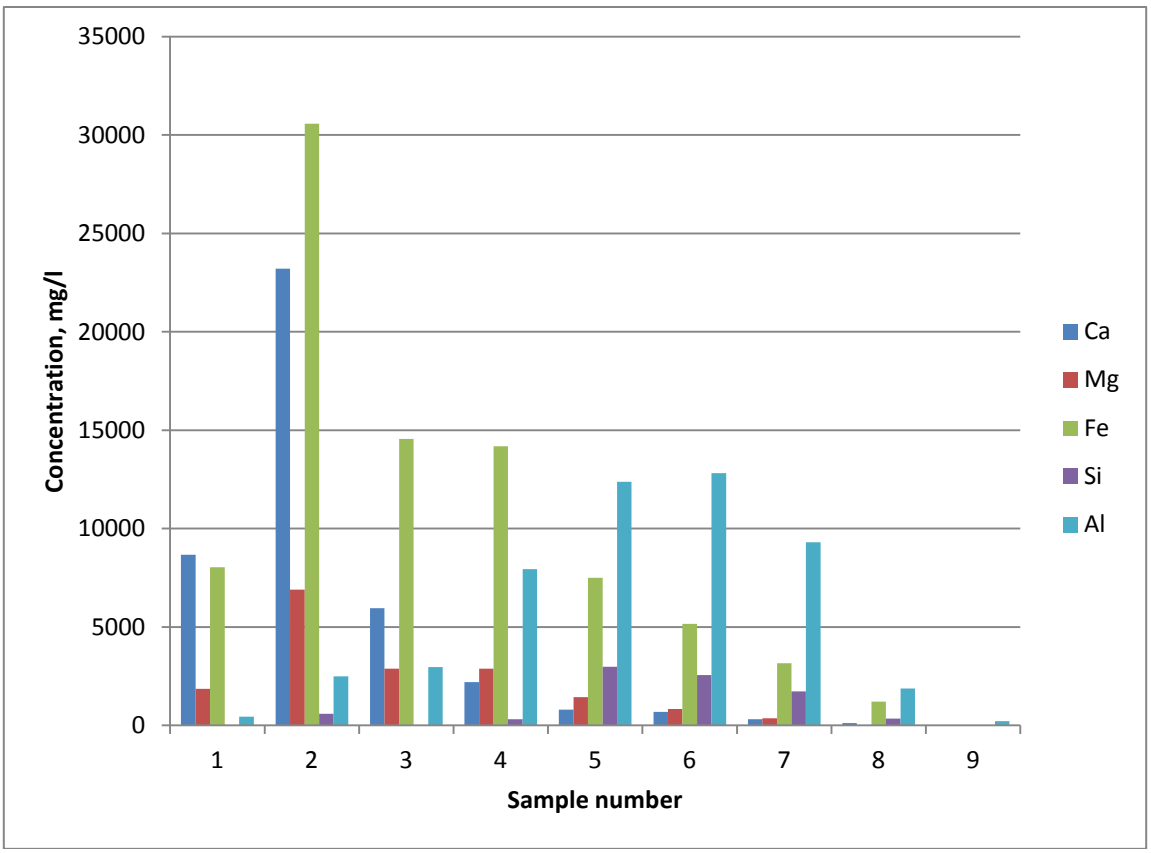

Fig. 5.14 ICP result of effluent experiment 5

Disscussion

Based on the work done, the following is observed and understood:

1. Experiments 4 and 5 were conducted using a HCl preflush, main acid stage was retarded mud acid and regular mud respectively and both experiments were conducted at the same flow rate and temperature – 300degF.
2. A permeability enhancement was observed in both experiments, for the regular mud acid there was a 60% enhancement, while the retarded mud acid yeilded at 64% permeability enhancement.
3. Even though the permeability ehancements are very close, this verifies that the added $AlCl_3$ to the formation does not affect the permeability enhancing capabilities of the HCl/HF combination by depositing unwanted materials.
4. On the contrary the addition of the $AlCl_3$ even enables a higher permability increase however slight.
5. The concentration of silicon in the effluent in both experiments show that for the treatment using AlRMHF, a maximum of 713mg/l of silicon was found in the effluent while for the treatment using RMHF, a maximum of 2973mg/l of silicon was found in the effluent – over 4 times the amount found in experiment 4.
6. Silicon in the effluent is an indication of dissolved sand grains during the acid treatment. This is undesirable because it means that sand would be produced during production (in an actual well) which can adversley affect

the completions causing erosion, well performance and also increase overhead cost of crude processing as sand in crude means extra effort for separation.

7. Fig. 5.15 below show a comparison of silicon concentration in the effluent when these two acids are used as the main acid stage.
8. In experiment 5 using RMHF as the main acid stage, a considerable amount of sand grains were also found on the coreholder outlet.
9. In the mineralogy analysis of the effluent samples from both experiments, it was also found that the rock treated with AlRMHF as the main acid stage contains less calcium than the rock treated with RMHF.
10. Next set of coreflood experiments are conducted varying acid flowrates.

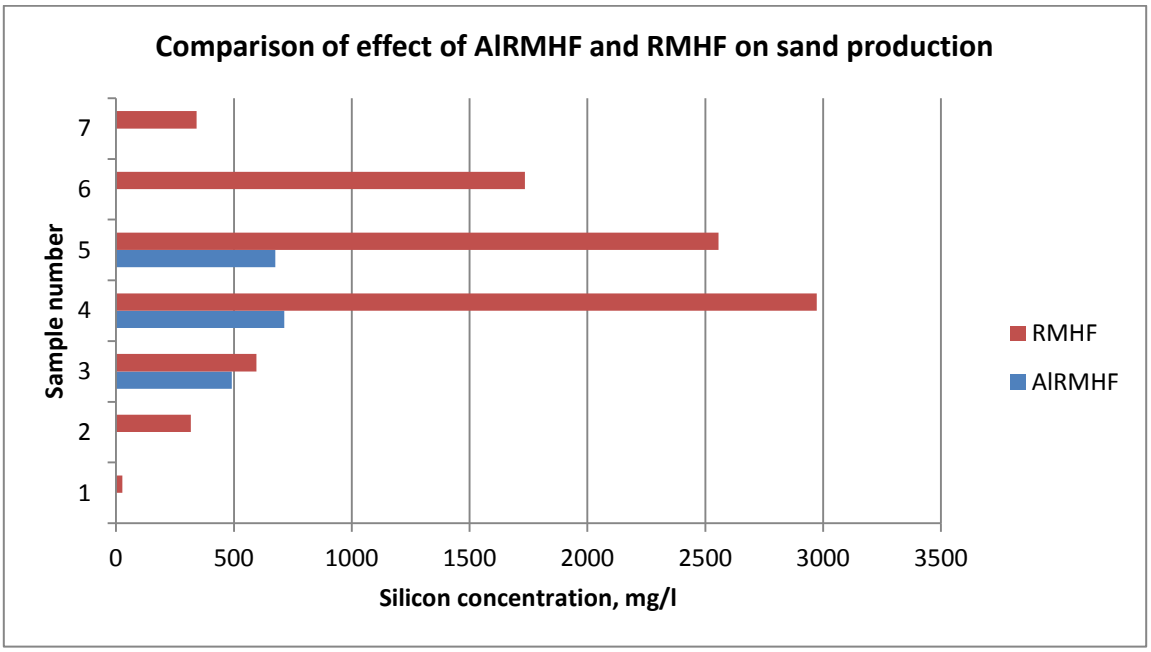

Fig. 5.15 Comparison of effect of AlRMHF and RMHF on sand production

5.2.6 COREFLOOD EXPERIMENT 6

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a regular mud acid (1.5wt%HF, 15wt%HCl)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 1cc/min

Initial permeability: 64md

Final permeability: 129.36md

Figs. 5.16 and 5.17 show the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and concentration of key ions from effluent samples from the ICP respectively.

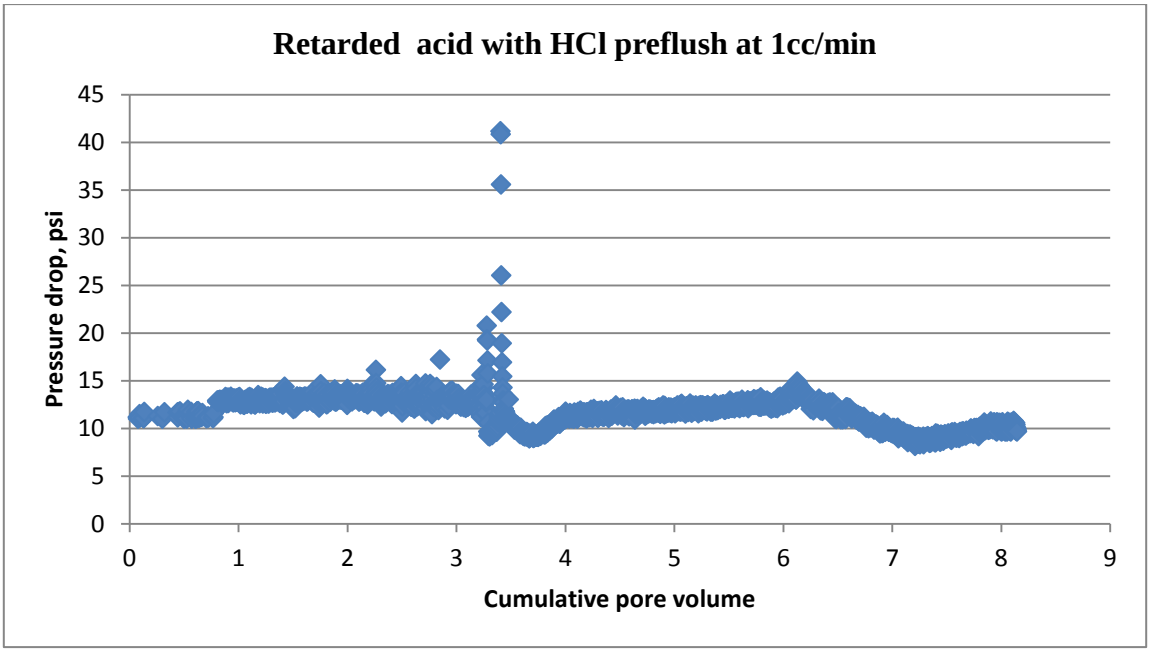

Fig. 5.16 Retarded mud acidizing with HCl preflush at 1cc/min

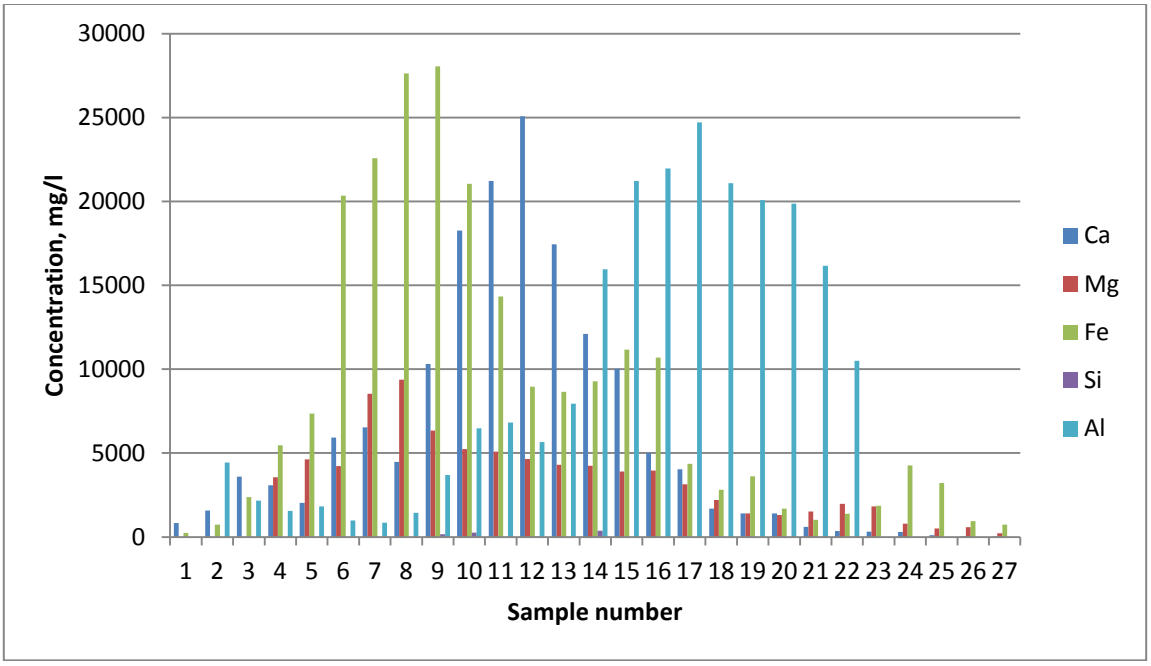

Fig. 5.17 ICP result of effluent experiment 6

5.2.7 COREFLOOD EXPERIMENT 7

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a regular mud acid (1.5wt%HF, 15wt%HCl)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 2cc/min

Initial permeability: 64md

Final permeability: 112.99md

Fig. 5.18 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.19 and Table 5.9 show the concentration of key ions from effluent samples from the ICP.

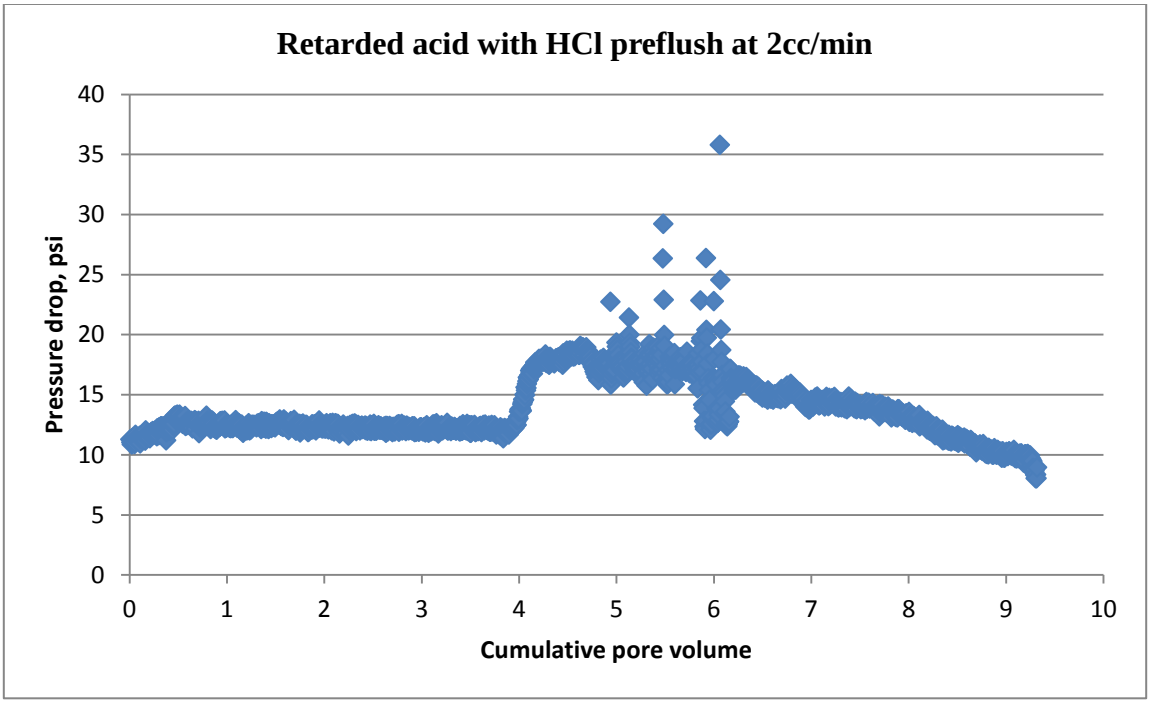

Fig. 5.18 Retarded mud acidizing with HCl preflush at 2cc/min

Table 5.9 Mineralogy of spent retarded acid at 300degF and 2cc/min

Ca	Mg	Fe	Si	Al
725	0	0	0	0
17240	5366	19960	211	2107
24160	9065	36610	847	6600
14430	5549	27340	575	4467
5703	2418	10890	0	2561
4540	2326	10280	0	6765
3230	1736	7807	0	11870
2747	1546	7215	0	18840
1750	1005	4944	0	18420
1413	823	4073	0	19160
893	477	2964	0	18060
584	291	2267	0	16160
300	0	1335	0	7569
449	0	969	0	1593

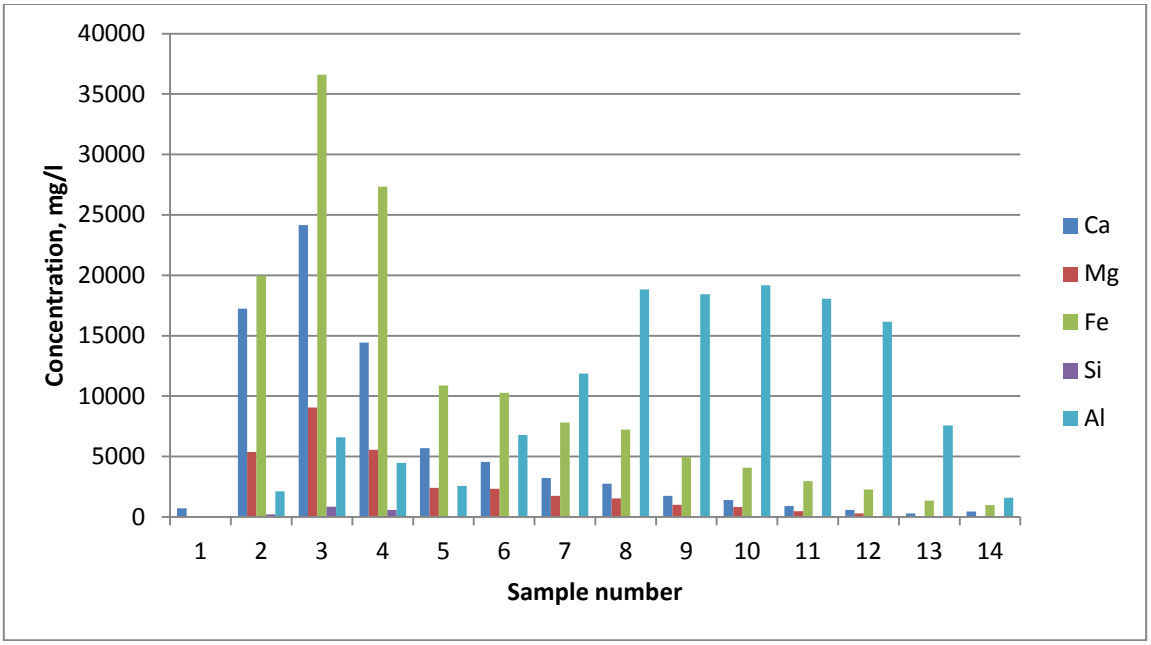

Fig. 5.19 ICP result of effluent experiment 7

5.2.8 COREFLOOD EXPERIMENT 8

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a regular mud acid (1.5wt%HF, 15wt%HCl)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 7cc/min

Initial permeability: 64md

Final permeability: 116.76md

Figs. 5.20 and 5.21 show the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and concentration of key ions from effluent samples from the ICP respectively.

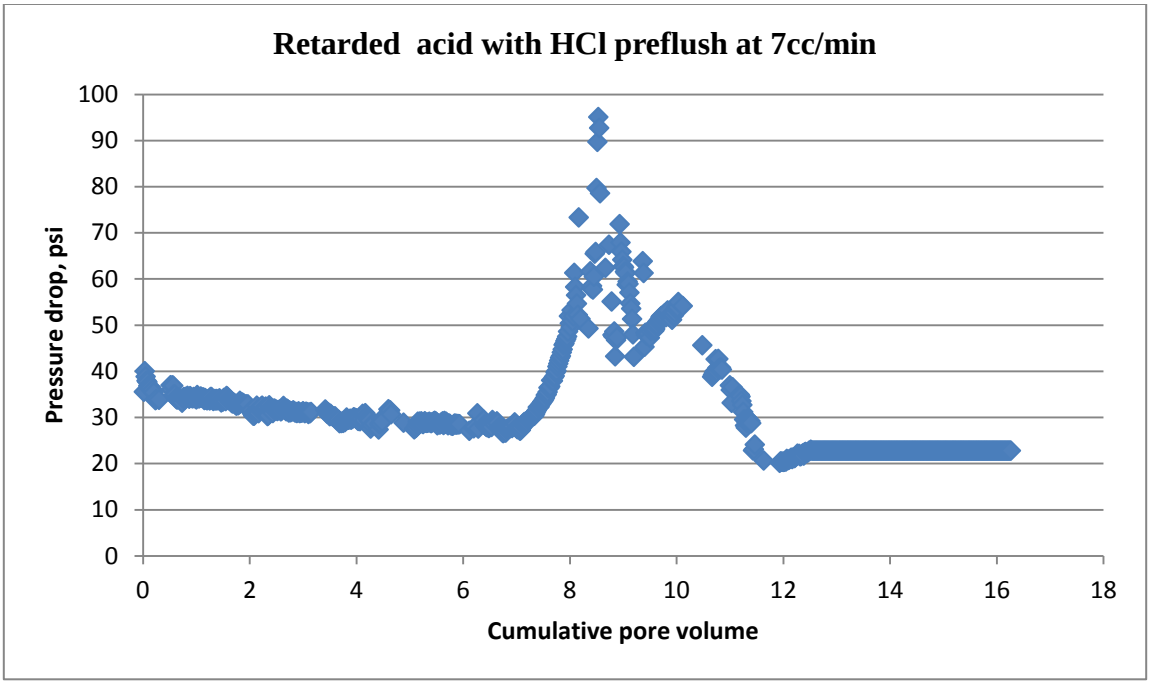

Fig. 5.20 Retarded mud acidizing with HCl preflush at 7cc/min

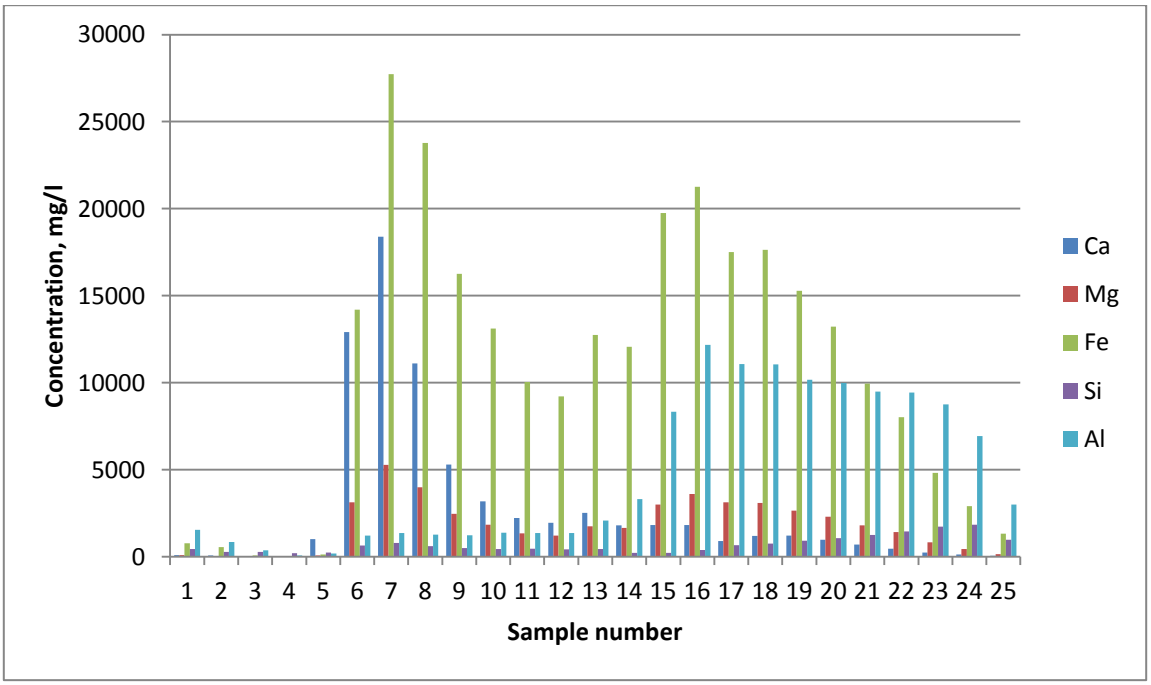

Fig. 5.21 ICP result of effluent experiment 8

5.2.9 COREFLOOD EXPERIMENT 9

Temperature – 300degF

Preflush – 15wt% HCl

Main acid – 2PV of a regular mud acid (1.5wt%HF, 15wt%HCl)

Postflush – 5wt% Ammonium chloride brine

Flow rate – 10cc/min

Initial permeability: 64md

Final permeability: 120.52md

Fig. 5.22 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.23 and Table 5.10 show the concentration of key ions from effluent samples from the ICP.

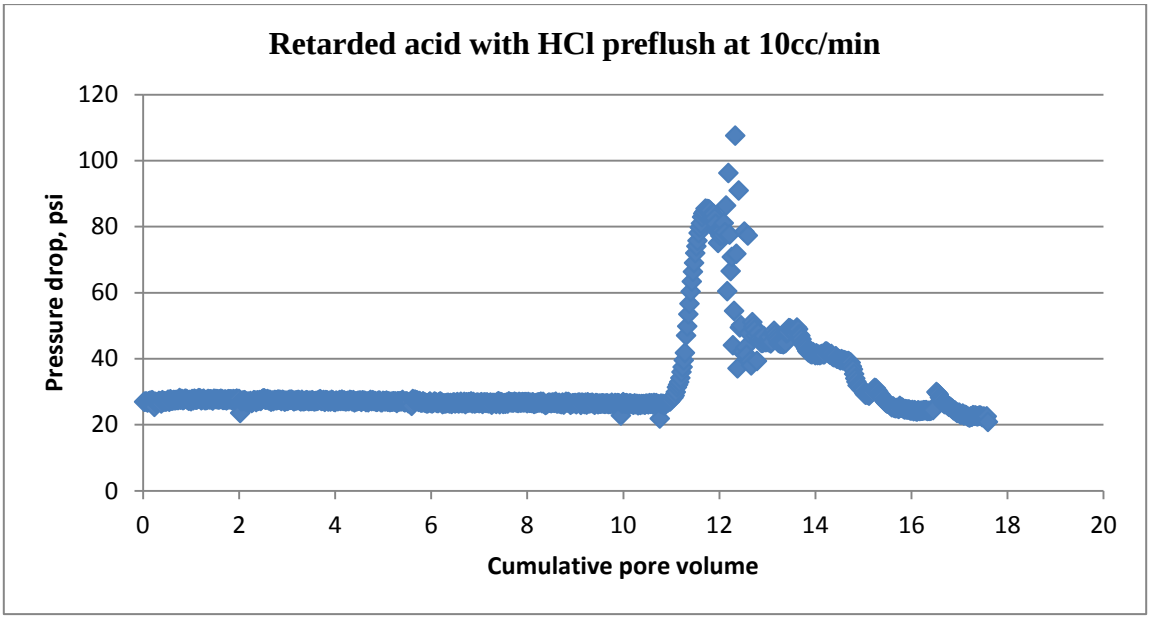

Fig. 5.22 Retarded mud acidizing with HCl preflush at 10cc/min

Table 5.10 Mineralogy of spent retarded acid at 300degF and 7cc/min

Ca	Mg	Fe	Si	Al
5401	863	3870	0	178
22100	6047	24170	377	1351
2919	1428	9275	9	1753
1620	1865	10660	0	4662
1064	3070	12750	867	10910
876	1256	6464	1865	10590
595	840	4708	1947	10090
304	338	2602	1664	3713
262	89	1400	24	907

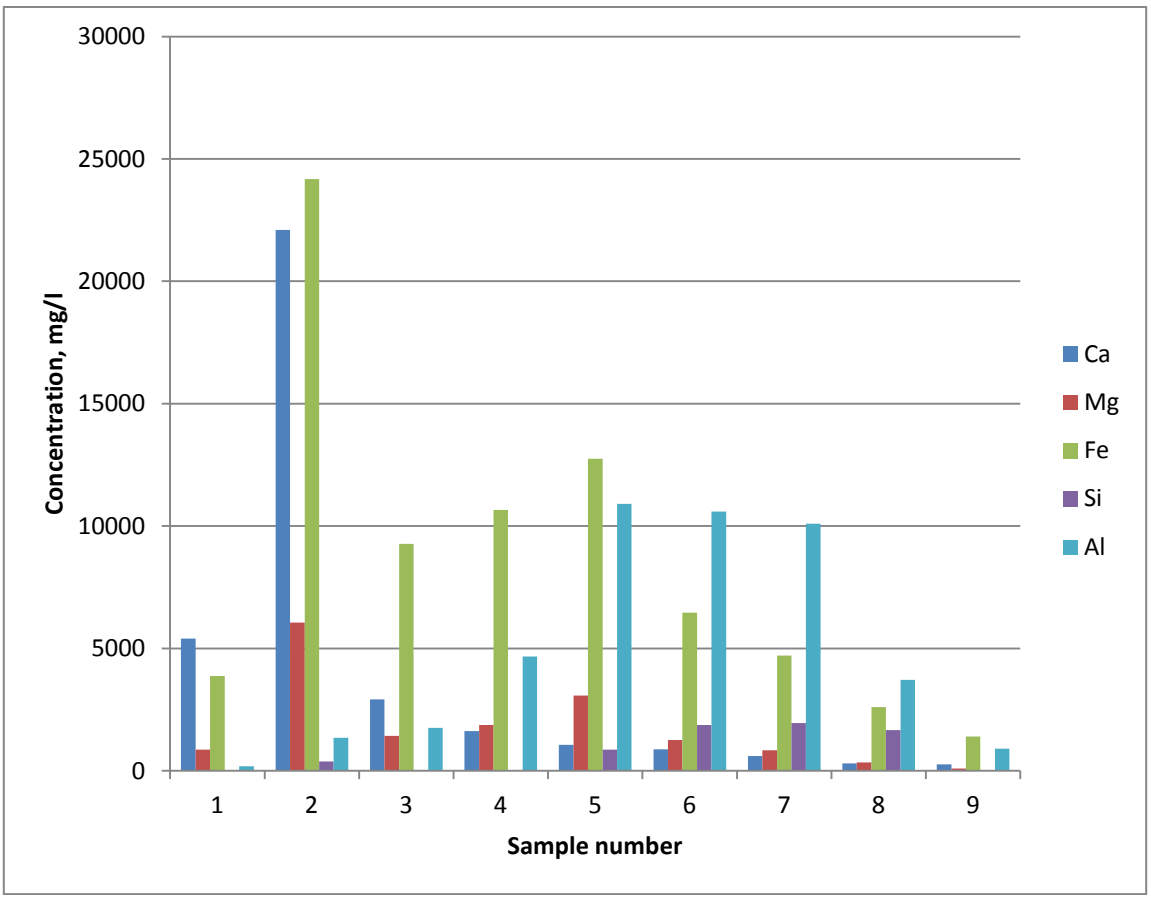

Fig. 5.23 ICP result of effluent experiment 9

Discussion

Based on the work done, the following is observed and understood;

1. Experiments 6, 7, 8, and 9 were conducted at 1cc/min, 2cc/min, 7cc/min and 10cc/min respectively to determine the effect of the retarded mud acid system using various flowrates.
2. With a flowrates of 1cc/min, 2cc/min, 7cc/min, and 10cc/min permeability increases of 102%, 77%, 82%, and 88% respectively occurred. Ratios of final to initial permabilities are shown in Fig. 5.24 for different flowrates.
3. These results indicate that a very low flowrate or a very high flowrate would result in the most permeability enhancement when a sandstone rock is acidized with a retarded mud acid system based on aluminum chloride
4. At a flowrate of 5cc/min the lowest permeability enhancement is observed.

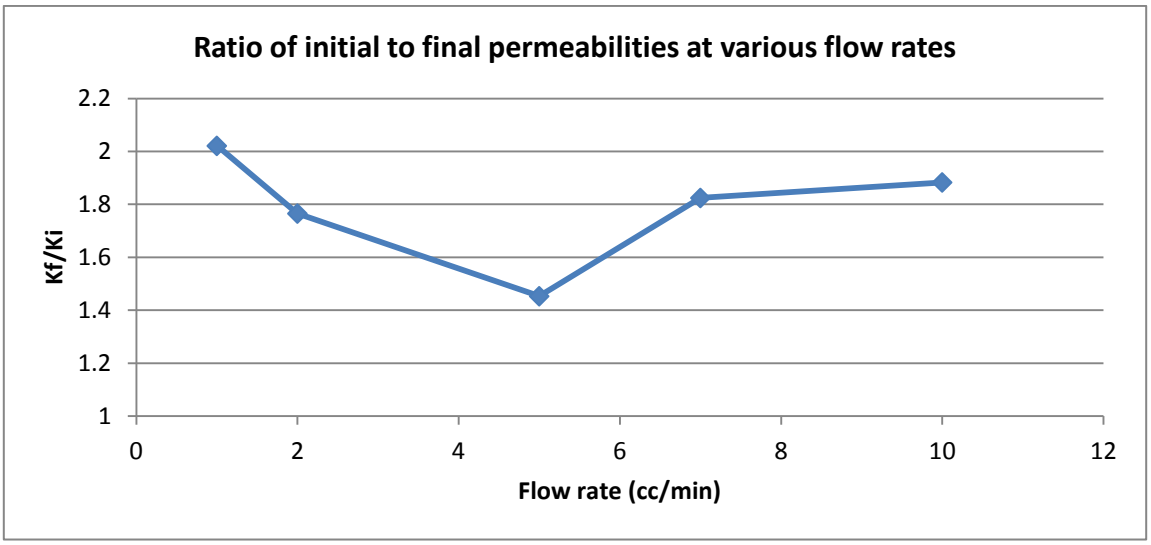

Fig. 5.24 Ratio of initial to final permeabilities at various flowrates

5. Examining the mineralogy of the effluent samples from the coreflood experiments shown in Figs 5.16, 5.19, 5.21 and 5.23 a very interesting trend is noticed.
6. At lower flowrates, a very little amount of silicon is evolved but as the flowrate increase the concentration of dissolved silicon increases considerably indicating that even though there is a very favorable permeability enhancement at theses high flowrates, the production of sand would eventually make the well economics highly unfavorable.
7. Aluminum concentration in effluent is also an important consideration. When acidizing with a retarded mud acid system based on aluminum chloride, aluminum is introduced into the formation and at unfavorable conditions, this trivalent cation can precipitate and affect the formation adversely. At 1cc/min a maximum aluminum concentration of 25,000mg/l was found in effluent and for 2cc/min, 7cc/min and 10cc/min, maximum aluminum concentration in effluent was 20,000mg/l, 13,000mg/l and 10,000mg/l respectively.
8. This indicates that some aluminum is being left in the formation and the lower the flowrate used in the acid treatment, the more aluminum and other metals flowback with the effluent from the rock.
9. Fig. 5.25 shows the maximum aluminum and silicon concentrations from effluent samples taken at various flow rates.
10. Calcium and magnesium concentrations in effluent are all relatively close and a lot of these metals are found in effluent samples collected during the

preflush indicating that the HCl preflush is properly removing carbonate materials that may be present in the sandstone rock.

11. The optimum flowrate for these set of experiments is found to be 1cc/min.
12. Majority of the iron in the effluent sample can be attributed to corrosion which occurs in the coreflood setup.
13. Next set of experiments are carried out introduing Fe(III) as an impurity to the acid system.

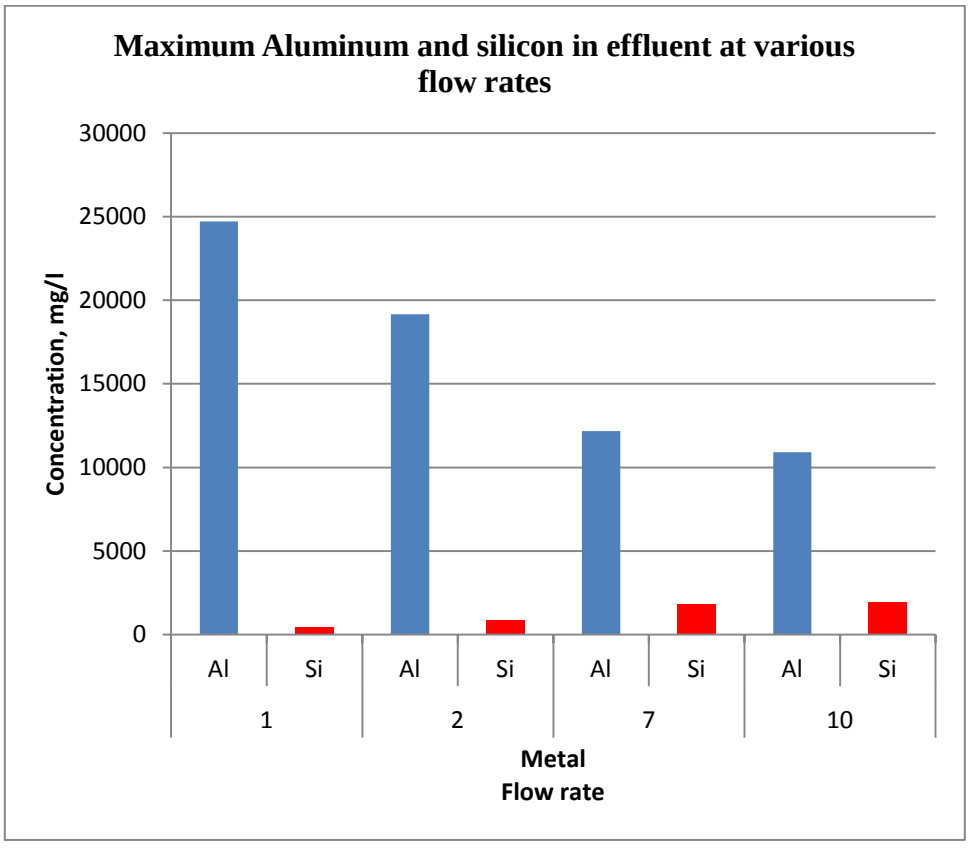

Fig. 5.25 Aluminum and siliscon comparison at various flowrates

5.2.10 COREFLOOD EXPERIMENT 10

Temperature – 150degF

Added impurity – 2000ppm Fe(III)

Preflush – 15wt% HCl

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Postflush – 5wt% Ammonium chloride brine

Flowrate – 5cc/min

Initial permeability: 64md

Final permeability: 76md

Fig. 5.26 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.27 and Table 5.11 show the concentration of key ions from effluent samples from the ICP.

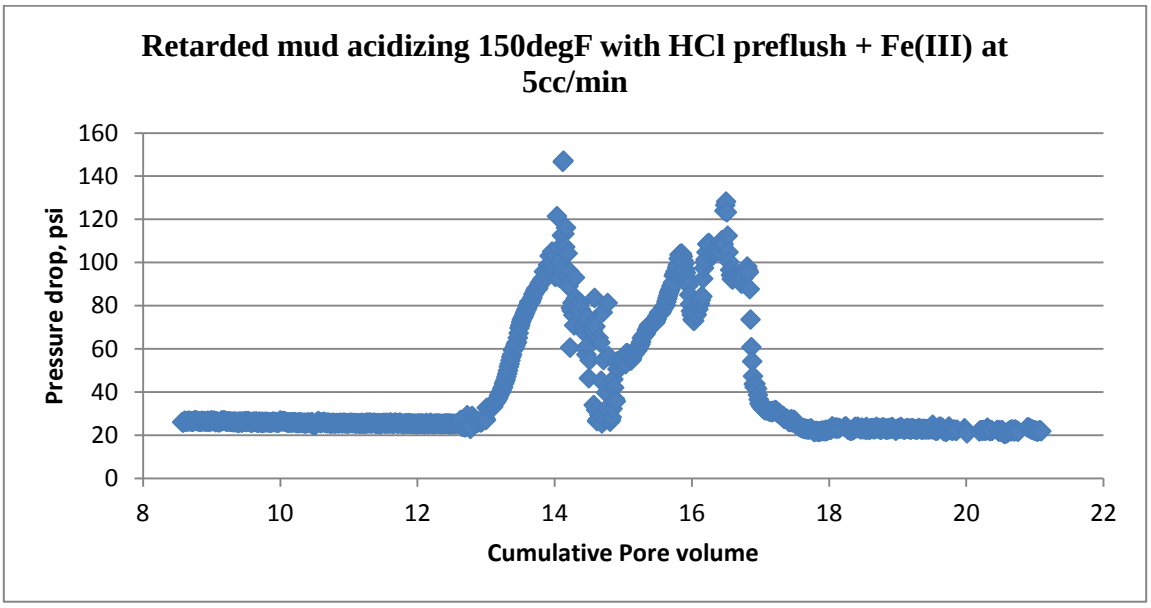

Fig. 5.26 Retarded mud acidizing 150degF with HCl preflush + Fe(III) at 5cc/min

Table 5.11 Mineralogy of spent retarded acid at 150degF with Fe(III)

Ca	Mg	Fe	Si	Al
7108	1348	4014	0	125
28510	6724	20140	0	319
12500	3398	13680	0	283
5318	2052	11700	0	2636
2065	2464	15720	335	7297
1032	2303	13920	1072	8130
491	1508	9420	1634	6438
23	214	2315	0	1348
0	0	410	0	289
0	0	0	0	112

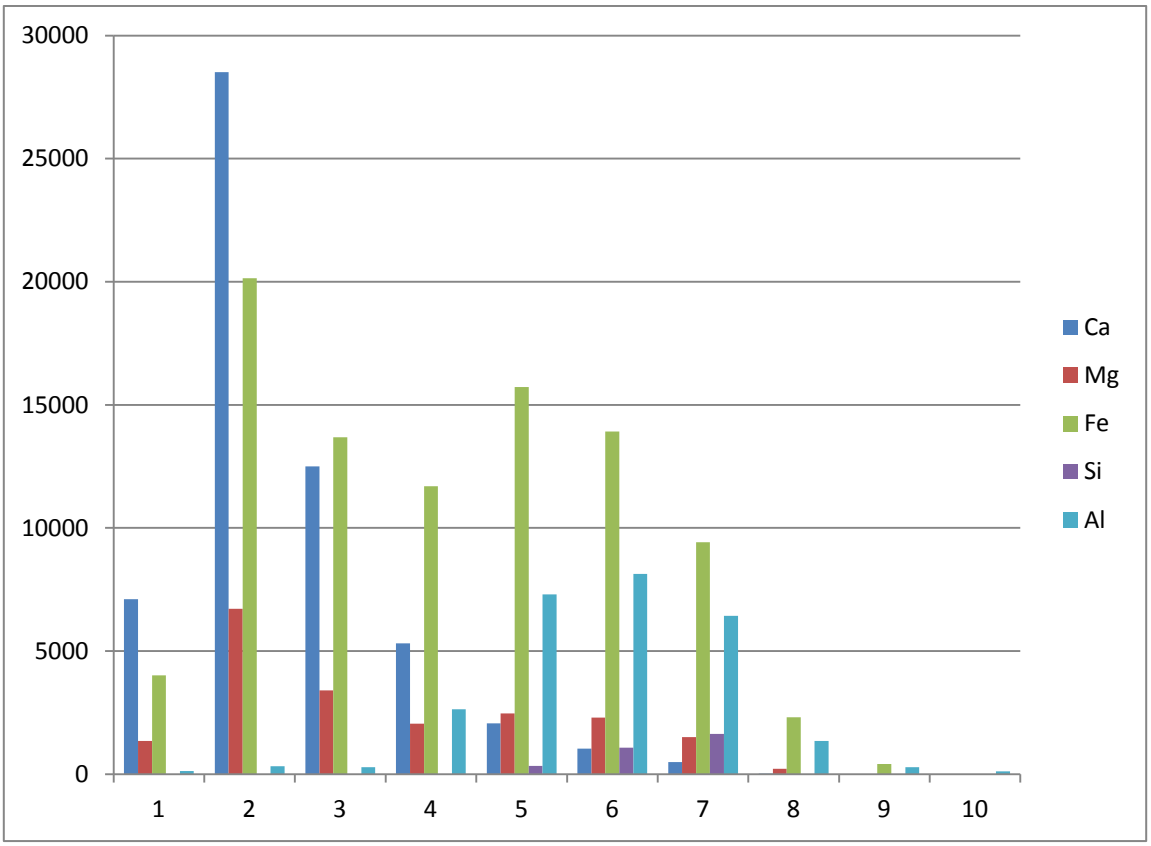

Fig. 5.27 ICP result of effluent experiment 10

5.2.11 COREFLOOD EXPERIMENT 11

Temperature 300degF

Impurity added – 2000ppm Fe(III)

Preflush – 15wt% HCl

Main acid – 2PV of a retarded mud acid (1.5wt%HF, 15wt%HCl and 5wt%$AlCl_3$)

Postflush – 5wt% Ammonium chloride brine

Flowrate – 5cc/min

Initial permeability: 64md

Final permeability: 70md

Fig. 5.28 shows the results from the coreflood experiment – pressure drop plotted against cumulative pore volume injected and Fig. 5.29 and Table 5.12 show the concentration of key ions from effluent samples from the ICP.

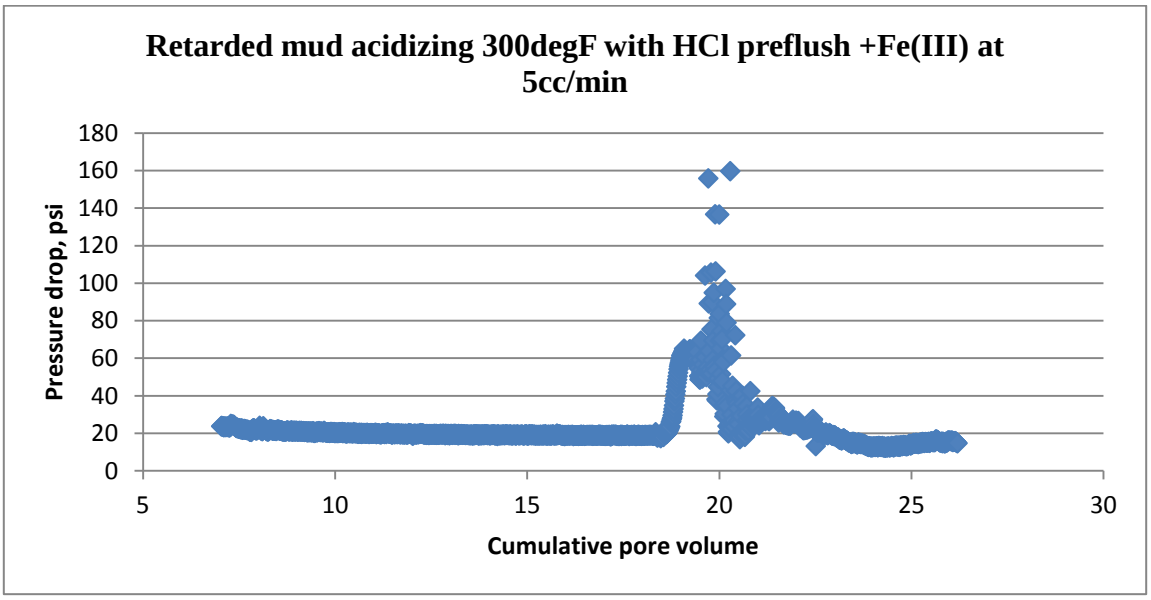

Fig. 5.28 Retarded mud acidizing 300degF with HCl preflush + Fe(III) at 5cc/min

Table 5.12 Mineralogy of spent retarded acid at 300degF with Fe(III)

Ca	Mg	Fe	Si	Al
5957	1175	5661	11	364
26470	7896	35920	853	2751
7921	3631	17540	0	3587
2325	2793	13020	0	5993
837	1861	9583	25	10940
482	824	5730	340	12080
730	369	3877	269	8388
0	0	191	0	627
0	0	0	0	25

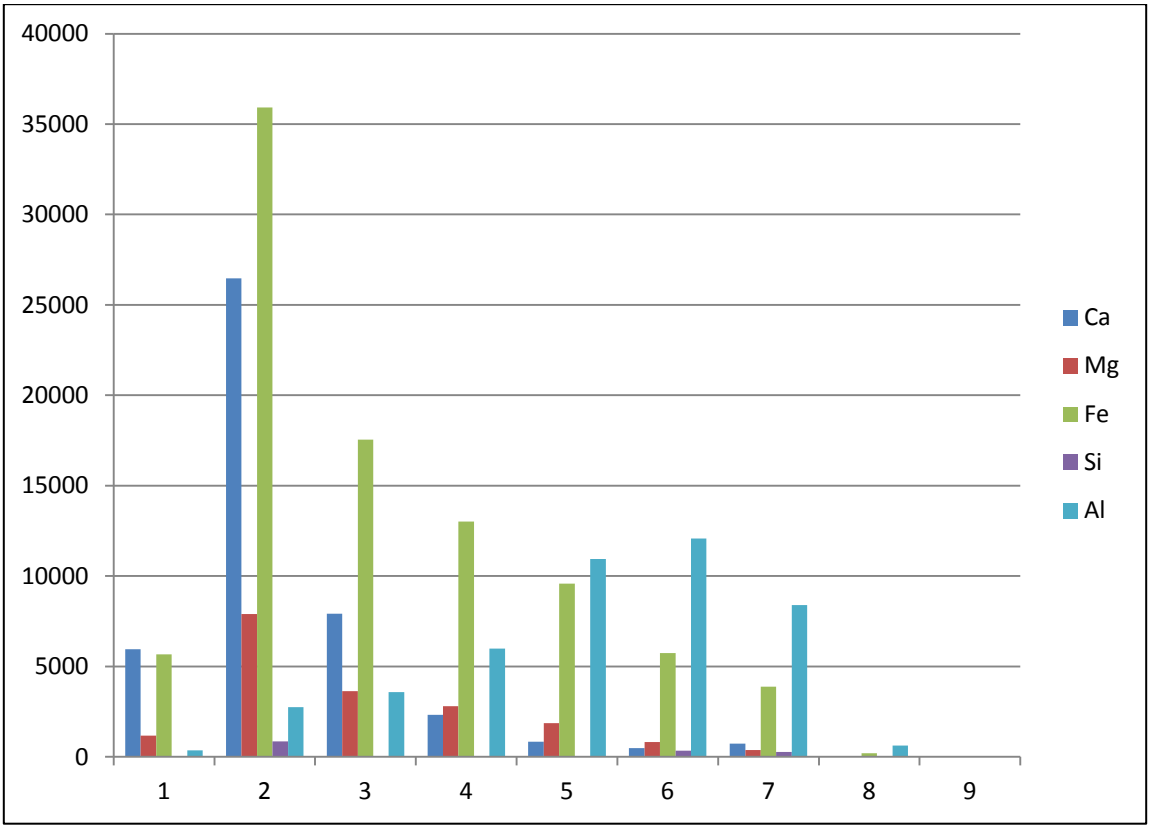

Fig. 5.29 ICP result of effluent experiment 11

Discussion

Based on the work done, the following is observed and understood:

1. Experiments 10 and 11 show coreflood experiments conducted with a retarded mud acid system based on aluminum chloride as the main acid stage and with an added impurity – 2000ppm Fe(III) performed at 2 temperatures – 150degF and 300degF respectively.
2. For the experiment performed at 150degF, a permeability enhancement of 19% was observed.
3. For the experiment performed at 300degF, a permeability enhancement of 9% was observed.
4. At 300degF, the permeability enhancement is half of what it is at 150degF showing that the presence of iron has a higher impact on the sandstone rock at elevated temperatures.
5. Even with the presence if iron(III) in the main aicd stage, there is still a permeability enhancement at these two temperatures however slight indicating that the retarded mud acid system is compatible with iron and does not adversley affect permability.
6. When compared with experiments 2 and 3 also conducted at 5cc/min, this shows that the absence of a HCl preflush is more detrimental to the sandstone rock than the presence of iron(III) as shown by the permeability loss in experiments 2 and 3 and permeability enhancement in experiments 10 and 11.

7. Mineralogy of effluent samples is consistent with other experiments conducted at the same temperature and no drastic difference is observed when iron is added except a slight increase in Fe concentration.
8. Coreflood experiments have been successfully conducted at various conditions. With and without a HCl preflush,with a retarded mud acid and regular mud acid as the main acid stage, with a HCl preflush at various flowrates, various temperatures and with added impurities.

5.3 pH OF SPENT ACID

1. It was observed after all the coreflood experiments, the pH of the spent acid was very acidic even more so than before the reaction.
2. This is due to the reaction of the injected acid with all the components of the sanstone rock.
3. Fig. 5.30 shows pH values representative of all the coreflood experiments. The highest pH values are observed at the beginning of the experiment when ammonium chloride brine is being injected into the sandstone rock which is basic. When the spent preflush and main acid stage start to come out from the outlet, the pH values drastically drop as can be seen in Fig. 5.30. Towards the end of the experiment as a post flush of ammonium chloride brine is injected into the formation, the pH values gradually begin to rise again as the effluent returns to a basic solution.

4. It was found that the onset of iron precipitation started at lower pH values, this could be attributed to any or a combination of the following reasons;
    - ✓ Fluoride ions forms a very stable complex with ferric ions
    - ✓ Ferric fluoride has a low solubility in water but is soluble in dilute HF
    - ✓ Most likely a portion of iron ions precipitated as an iron fluoride complex (FeF_6)

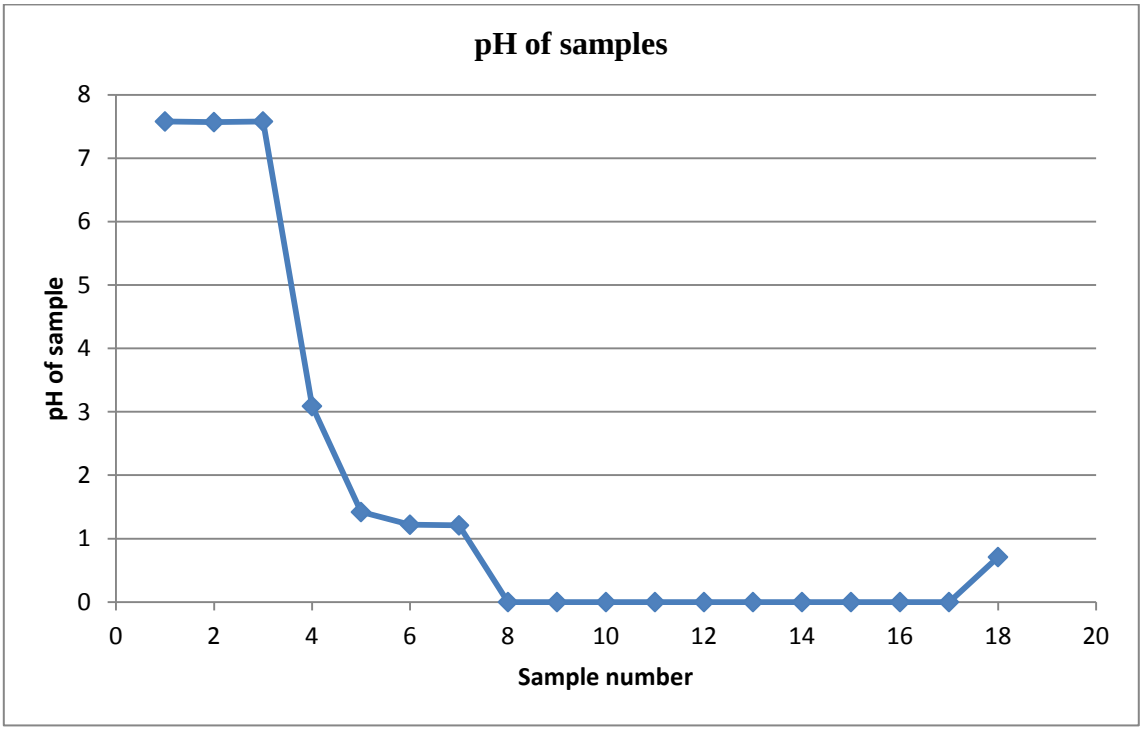

Fig. 5.30 pH of samples

5.4 ACID CONCENTRATION IN EFFLUENT

The acid concentration of effleunet samples from the core flood analysis at different conditions was titrated using a sodium hydroxide base to determine the acid concentration in different samples and the follwing were observed.

1. Acid concentration in all the samples at various conditions are approximately the same - they all maxed out on very close numbers.
2. Injected acid concentration is approimately 4.4mol/l
3. Maximum final acid concentration is approximately 4.8mol/l
4. This is an indication that all the HCl injected was present in flowback and the HF was completely consumed in the reaction.
5. Figs. 5.31 and 5.32 show representative acid concentration from experiments with flowrates of 1cc/min and 7cc/min. A similar trend was found in all the other experiments.

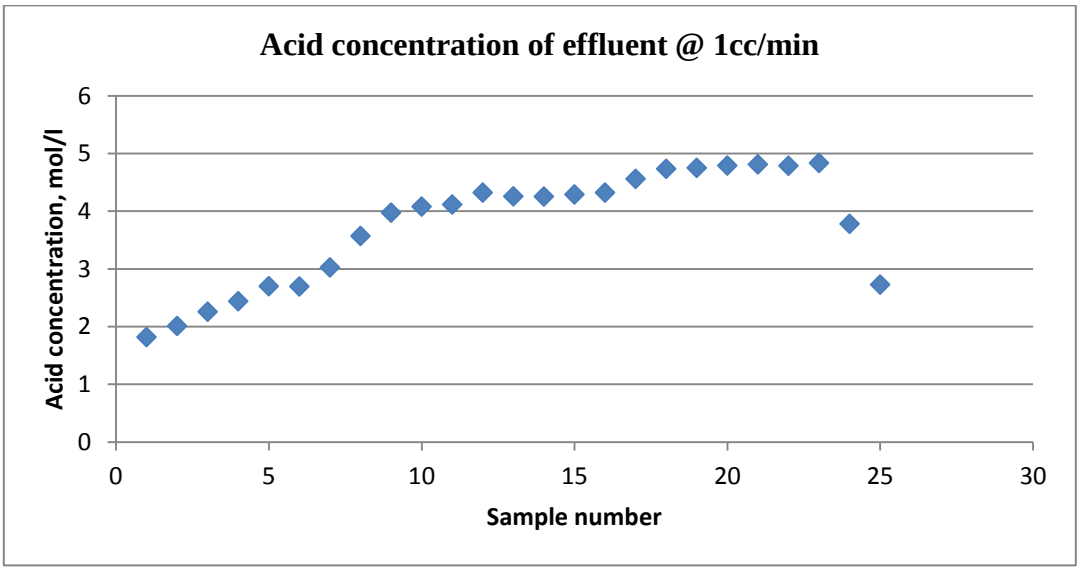

Fig. 5.31 Acid concentration of effluent at 1cc/min

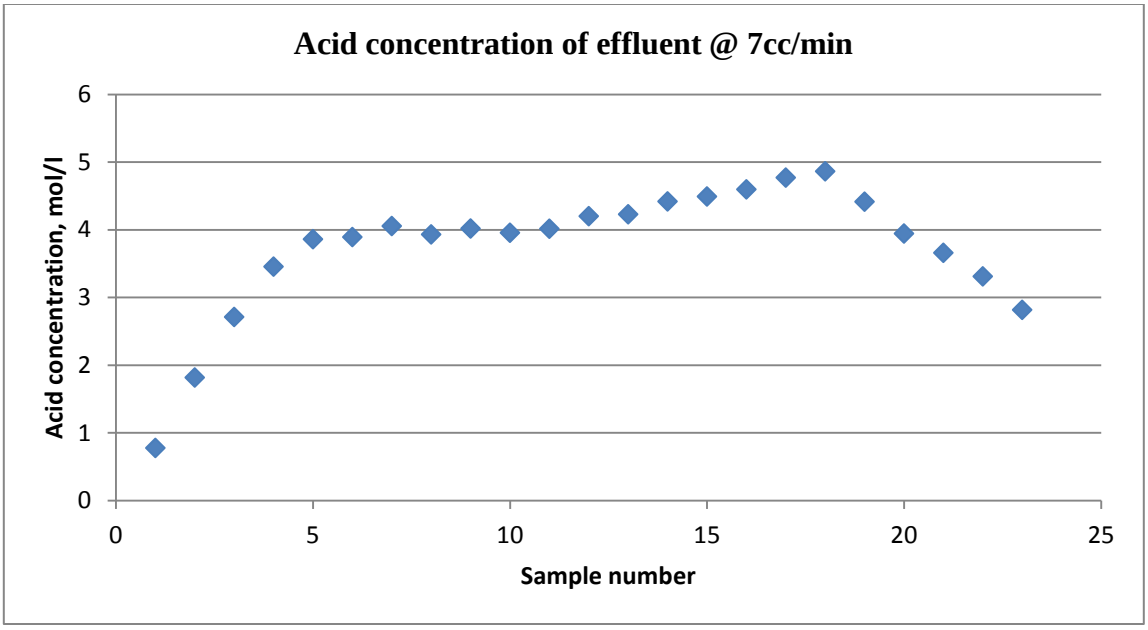

Fig. 5.32 Acid concentration of effluent at 7cc/min

5.5 DISSOLUTION REACTION

This experiment was conducted to determine the reactivity of the retarded mud acid system over regular mud acid.

1. After dissolving the rock with a starting rock weight of 43.011g, weight lost from the retarded acid based on aluminum chloride was 0.28% while weight lost from the regualr mud acid was 0.84% as shown in Fig. 5.33.
2. This means that the regular mud acid would dissolve the rock almost 3 times as fast as the retarded mud acid would.
3. This also means that the retarded mud acid is less reactive over the time frame of the experiment.

4. A slower rate of reaction means a deeper acid penetration and deeper damage removal.

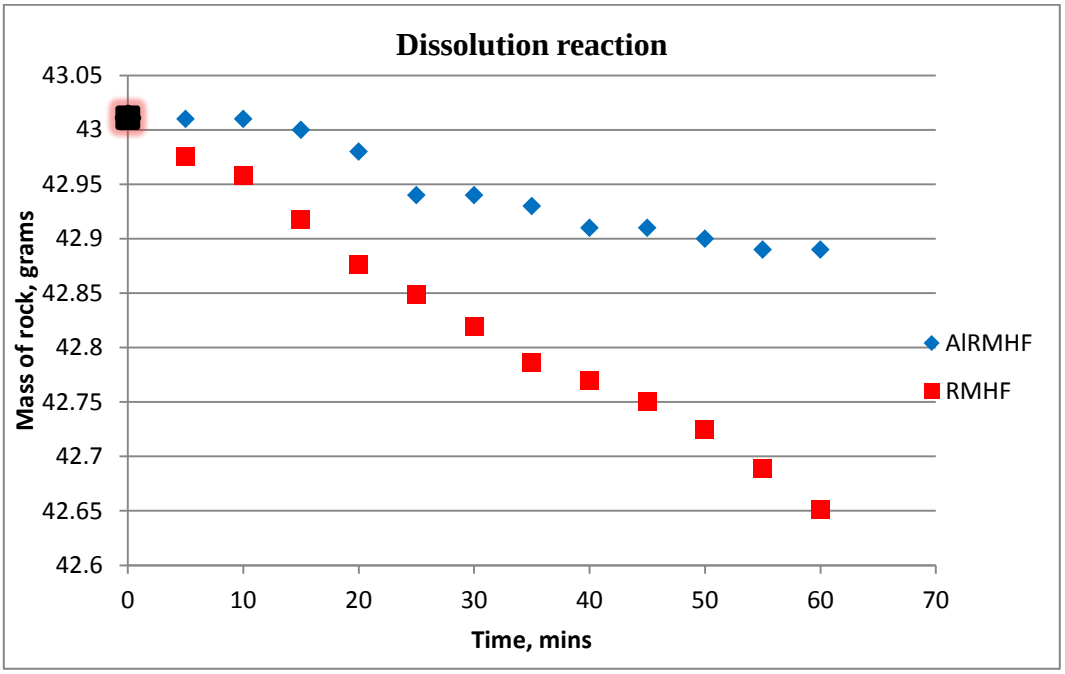

Fig. 5.33 Dissolution of sandstone rock

5. Examining the mineralogy with respect to time, it was also observed that over the 60mins interval of the experiment, the amount of silicon dissolved is the regular mud acid system is almost twice of the amount in the retarded mud acid systen.
6. On the other hand, the amount of calcium dissolved from the sandstone rock due to the regular mud acid is half the amount dissolved as a result of the retarded mud acid system.
7. This indicates that AlRMHF reacts with $CaCO_3$ more than RMHF.

8. Al-Dahlan in 2001, SPE 65032 found the concentration of Calcium to double when different clays were reacted with AlRMHF when compared to RMHF.
9. RMHF reacts more with Silicon than AlRMHF.
10. Silicon and calcium concentrations for the two acid systems are shown in Figures 5.34 and 5.35 respectively.
11. Table 5.13 shows dissolved elements present in acid after reaction with the rock.

Table 5.13 Mineralogy from dissolution reaction

	AlRMHF (mg/l)			RMHF (mg/l)		
Time, min	Silicon	Calcium	Aluminum	Silicon	Calcium	Aluminum
5	100	78	3661	724	64	155
10	372	106	3754	760	71	110
15	418	140	3713	842	82	131
20	433	147	3483	908	83	117
25	453	182	3743	1073	102	146
30	457	207	3851	1075	102	150
35	462	218	3869	1087	116	137
40	474	252	3948	1110	121	149
45	501	247	3787	1228	123	150
50	623	275	3875	1351	118	163
55	643	295	3966	1364	132	173
60	752	293	3831	1413	146	169

12. For the AlRMHF the high aluminum concentrations are as a result of the acid retardant – $AlCl_3$.

13. Nasr-El-Din et al. SPE 73747, 2002 found that the Al concentration in prepared retarded acid systems were 3932mg/l and 3752mg/l which is in agreement with the freshly preparded retarded acid having a concentration of 3827mg/l.
14. It is also important to note that the dissolution experiment was aimed at comparing conventionally used retarded acid based on $AlCl_3$ with conventionally used regular acid. As a result experiments could produce different results if the same amount of HF is used for both experiments. For the retarded acid system, HF concentration is 1.5wt% and for the regular acid system, HF concentration is 3wt%.

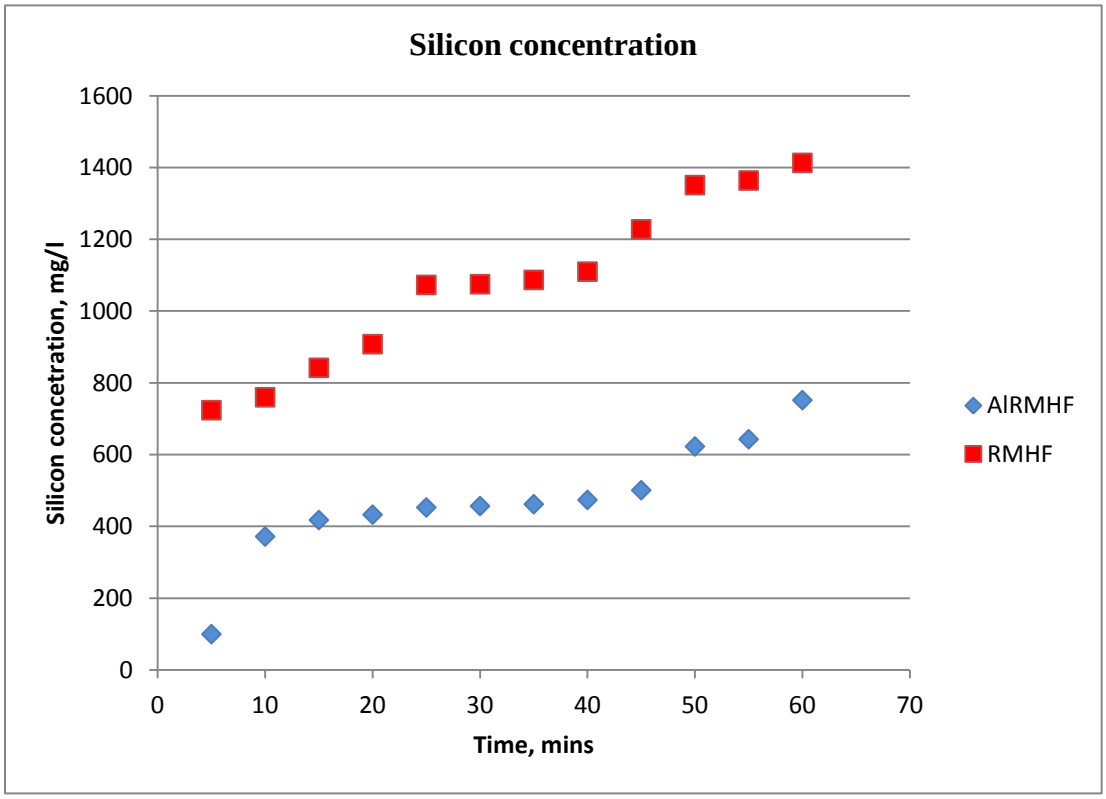

Fig. 5.34 Silicon concentration

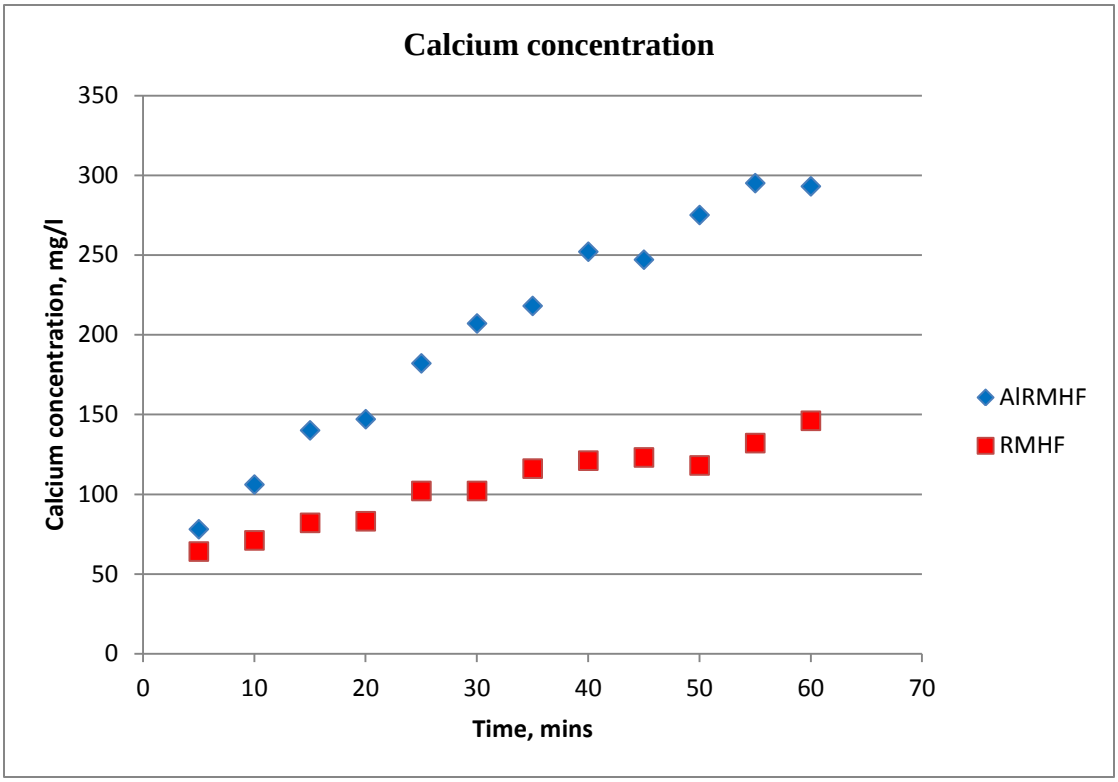

Fig. 5.35 Calcium concentration

CHAPTER VI

CONCLUSIONS

6.1 SUMMARY

The following can be summarized from the work done on the investigation of a retarded mud acid system.

1. The absence of a HCl preflush is detrimental to the sandstone core as calcium fluoride is precipitated as shown in coreflood experiments 2 and 3. With the damage being more as the temperature increases.
2. The retarded acid system is compatible with iron(III) as an impurity. There is a permeability enhancement in the core and the retarded acid is not compromised.
3. Permeability enhancement is approximately the same for a cores acidized with retarded and regular mud acid at the same flow rate, with the enhancement for a retarded system being slightly more.
4. The mineralogy on the other hand is very different. The RMHF dissolves considerably more silicon and produces more fines than the AlRMHF.
5. 1cc/min was found to be the optimum flowrate when a sandstone core is acidized with AlRMHF.
6. At this low flowrate; less silicon is dissolved, more aluminum is seen in the effluent and more calcium is dissolved.
7. All the HCl injected into the core comes out with the effluent samples and none of it is retained in the sandstone core, which is an indication of a good acid treatment.

8. The retarded Aluminum acid system considerably reduces the rate of reaction as evidenced in the dissolution reaction when compared to a regular mud acid system.
9. This reduced rate of reaction implies deeper acid penetration and ultimately deeper damage removal.

6.2 RECOMMENDATIONS

1. Any acid system should be properly investigated for compatibilty with the formation of rock before the onset of acidizing.
2. The AlRMHF should be further investigated to determine its compatibility with very high (such as boise sandstone) and very low (such as bandera sandstone) permeabilty rocks.
3. The lower the flowrate the better the rock quality after acidizing in terms of dissolved solids and fines production.
4. Other retardants should be investigated – Boric and phosphonic acid.
5. NMR spectroscopy should be conducted on samples to determine mineral complexes.

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